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Oceanic Gas Hydrate: Guidance for Research and Programmatic Development at the Naval Research Laboratory

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<p>The Naval Research Laboratory (NRL) is assembling an internal research thrust concerning the distribution, materials properties, chemistry, and influence on naval operations of methane hydrate. Methane hydrate is a naturally occurring crystalline assemblage of water and methane molecules. Water molecules form a rigid cage-like structure which traps methane in voids internal to the cage. This report documents output from a workshop covered at NRL to provide guidance on the structure and focus of the proposed research thrust.</p>			
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Oceanic Gas Hydrate: Guidance for Research and Programmatic Development at the Naval Research Laboratory

M.D. Max, R.E. Pellenbarg & B.B. Rath

Part 1. Program development and recommendations

Executive Summary

The Naval Research Laboratory (NRL), a leading research institution in the United States, has identified oceanic gas hydrate and methane flux from seafloor sediments as one of the emerging fields of scientific research related to the world's oceans. Oceanic gas hydrate, a crystalline material formed from mainly methane and water that is deposited in the pore spaces in marine sediments below about 500 m water depth, appears to occur in huge quantities in seafloor sediments. Gas hydrate is presently attracting attention because it has been recognized as a potential source of methane fuel, with two countries, Japan and India, having already established national research programs dedicated to the economic recovery of methane from seafloor hydrate deposits. However, hydrate and its reaction to methane flux and changing ocean pressure-temperature conditions also appears to be an important factor in seafloor stability, ocean carbon cycling, biological productivity at the base of the food chain, and global climate change. The primary impact of hydrates upon the Navy is that its presence in marine sediments alters the physical properties of the seafloor and affects acoustic propagation at frequencies of interest for detecting submerged objects. In addition, its presence may have an impact upon the location and security of seafloor-mounted Navy instrumentation and seafloor engineering artifacts. Further, methane can be used as a basic fuel, and feedstock for higher molecular weight organic compounds, for naval application.

Oceanic gas (methane) hydrates were only observed in seafloor sediments in the late 1960s, but they comprise an important research field because of their now apparent immense volume and widespread distribution. Much remains to be discovered about hydrates, a situation which necessitates the development of a comprehensive gas hydrate research program. As part of the process of developing this program, NRL has begun to marshal its internal resources to broaden its ongoing gas hydrate research activities, in which NRL already has a record of innovation, activity, and publication.

To facilitate the process of program development, Dr. B.B. Rath, of the NRL technical directorate, initiated a workshop designed to bring an interdisciplinary team of scientists into the gas hydrate field and broaden NRL's existing program, which was based on field activities, development of new technology, and geological and geophysical modeling. To remain at the forefront of innovation, it is necessary to develop numerical approaches to characterizing the material properties of natural and synthetic hydrate and its affect on the marine sediments in which it forms. Leading scientists from outside NRL were invited to attend the workshop, with a view to observing and commenting upon NRL resources and personnel, to form a body of external expert knowledge and opinion that

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would not only help identify the main research issues, but to focus development of the NRL gas hydrate program on those NRL attributes that offered the most immediate likelihood of greatest success.

The NRL program development is intended to be broad, extending across a wide span of NRL scientific expertise and capabilities, but also deep, extending from conducting basic research to producing relevant information leading to commercial activities. The main object of the workshop, however, was to develop a gas hydrate research program that would both produce excellent science and raise non-Navy support. In particular, those agencies, institutions, and companies that are mainly driven by the primary economic objective of recovering methane from gas hydrates have been identified as emerging sources of funding to support NRL scientific endeavors.

The process of identifying the main science issues, upon which could be brought to bear the scientific resources of NRL, were successfully begun during the workshop. A hydrate program was outlined, external potential joint research participants were identified, and interaction with representatives of two potential funding agencies attending the workshop as observers allowed shaping the research effort to satisfy potential sponsor needs. This report summarizes the main gas hydrate issues and presents the results of two workgroups, one of which was focused on the marine science issues of hydrates while the other concerned itself more with NRL research issues that pertained to development of a hydrate research program. Three integrated scientific-practical (economic) fields are defined as the basis for the expanded NRL gas hydrate research program.

Basis for a U.S. gas hydrate research program

Establishment and development of the basis of a national gas hydrate research program has been recognized in the Presidents' Committee of Advisors on Science and Technology report concerned with energy, published on 30 September, 1997, in a strong, positive statement. ("... the Panel recommends more intense effort on natural gas production and processing, including a major initiative for DOE to work with USGS, the Naval Research Lab, Mineral Management Services, and the industry to evaluate the production potential of methane hydrates in U.S. coastal waters and world wide"). Bill S. 1418, a bill to promote the research, identification, assessment, exploration, and development of methane hydrate resources, and for other purposes; to the Committee on Energy and Natural Resources, The methane hydrate research and development act of 1997 was read into the Congressional record on 7 November, 1997. It directs, "the Department of Energy to conduct research and development in collaboration with the Naval Research Laboratory and the U.S. Geological Survey." NRL is actively involved with the development of the DOE program. Development of an NRL gas hydrate research program must be structured to support not only basic science of interest to the Navy, but to respond to this bill when it becomes law.

Strategy for NRL gas hydrate research program

The Naval Research Laboratory (NRL) has a very broad scientific program in support of Navy science and technology objectives. NRL operates both in the field and in the laboratory, and is concerned with all aspects of the basic sciences and advanced exploratory development covering a spectrum of operations from below the seafloor to outer space. As a major scientific laboratory concerned with discovering new scientific information that may allow for currently unforeseen Navy applications, NRL has identified oceanic gas hydrates as a significant new research field in ocean sciences.

Oceanic gas hydrate was first reported in seafloor sediments in the late 1960's. Hydrates in the sediment reside in a hydrate stability zone (HSZ) that exists from the seafloor down to a sub-seafloor depth where ambient temperature has increased to a level where the phase boundary limit for gas hydrate stability is reached. The base of the HSZ is approximately parallel to the seafloor because isotherms commonly are parallel the seafloor (Max et al., 1997). At a constant geothermal gradient, the HSZ is thicker at greater water depths. The Hydrate Economic Zone (HEZ) is the entire zone that may be important to recovery of methane. It includes the HSZ and subjacent gas zones and pore fluid zones that are gas rich. In an area where sedimentation has continued over a long period of time, hydrate at the base of the hydrate layer may become unstable and dissociate. Where this happens, the hydrate conservation cycle, which is a steady state, process for concentrating methane operates. Gas produced in or below sediment from dissociated hydrate will rise through buoyancy and tend to again form gas hydrate.

Only recently has it been realized that the amount of hydrate in continental margin and ocean basin sediments is extremely large and that the hydrate is a major factor in the earth's global carbon budget (Max et al., 1997). Further, if hydrate can be developed as an energy source, the impact of the availability of major new methane supplies has the

potential to alter global fuel choices and CO₂ emissions, and affect the geopolitical world order. Gas hydrates are a scientific field that can best be approached through a broad-based, integrated research program, because much of the basic research knowledge is likely to be obtained from a number of specialist research topics. Although previous attempts to formulate a national program in gas hydrate research proved immature (Max et al., 1991a, 1991b), US-based scientists still retain the lead in world-wide gas hydrate research despite a difficult funding environment. The situation, however, is changing rapidly. The United States no longer has the initiative in gas hydrate research. In the last six years, a number of developments have brought oceanic gas hydrate to the forefront of research in a number of countries, with a consequent injection of funding for research that is increasingly being supplied by non-U.S. entities (Appendix 1).

NRL is developing an expanded gas hydrate research program, with due attention to developments in other government agencies, industry, and foreign countries. It can be seen from the plethora of scientific issues associated with hydrates (Appendix 4, 5) that, selection of the most important scientific elements is difficult without some external reference. Thus, we have identified three integrated Scientific/Economic fields (Table 1) and the primary scientific approaches relevant to each, rather than focusing on the science issues alone. It is important to note that this report is only an outline for the initiation of an expanded hydrate research program. Substantial program growth is anticipated, both in the variety of the scientific activity and in the definition of new Sci/Econ topics which may develop as the program proceeds. Determination of the most relevant science issues for each topic remain to be more fully developed. Because the Sci/Econ topics are closely related, as are many gas hydrate issues, there is some overlap between them. Each, however, provides a very different and separate focus upon which scientific inquiry can be brought to bear.

Scientific/Economic Field	Thrust of Research	Approach
1. 3-D characterization of HEZ, methane distribution and concentrations in both hydrate and free gas	Physical properties of hydrate-affected sediment, Reservoir integrity, volumetric analysis	Multi-channel seismic analysis, seafloor imagery, geological and geophysical modeling, biochemical analysis
2., Geological history of deposit, degree of maturity, Hydrate conservation cycle	Maturity of deposit, likelihood of economic development	Age dating, fluid flow modeling, in-situ gas measurements, geological modeling, biochemical analysis
3. Dissociation characteristics, gas flux in HEZ	Kinetics of gas formation from hydrate and metastability within HSZ	Thermodynamics, crystallography, laboratory analog experiments

Table 1. Outline of the first-order elements of the proposed NRL integrated gas hydrate research program.

1. The most fundamental unknowns of hydrates and methane in the seafloor regime

are how much is there, how is it distributed, and how has it altered physical properties of the marine sediment in which it forms. This information is broadly relevant across energy, global climate, seafloor stability, and the possibility of economic development.

2. The hydrate conservation cycle (Lowrie and Max, 1996) is the long-term process of methane concentration in which hydrate at the base of the HSZ gasifies during periods of sedimentation that raise the level of the seafloor. The gas then tends to either be trapped or pass upward into the elevated HSZ, where much of it will form new hydrate. Where the cycle has operated for a long time, the deposit is likely to be enriched in methane and characterized as 'mature'. Where the cycle has not operated because of insufficient methane flux or capture within the HSZ, the deposit is not enriched and can be regarded as 'immature'. Both the formation and dissociation characteristics of hydrate are important. The in-situ rates of methane distribution and redistribution are most important, and, in fact, are largely unknown at this time.

3. This topic focuses on the physical and crystal chemistry of the hydrate reaction and its fields of stability with respect to conditions in both the natural environment and the laboratory. The results of these studies support refinement of the individual hydrate formation and conservation cycle histories of individual deposits, which are known to be different in detail, and provide the basic information relevant to economic exploitation of hydrate in combined hydrate-gas deposits. Geochemical/chemical analysis has the potential to assist in calibration and confirmation of acoustic analysis. The dynamics of methane chemistry and thermodynamics is a fundamental issue that will have significant impact upon virtually all aspects of the oceanic hydrate system.

Although the majority of hydrate-focused work in NRL to date has been carried out by the Marine Geoscientists (NRL Division Code 7400), it is imperative that personnel from the Materials Science and Component Technology Directorate (Code 6000) are brought into the developing NRL gas hydrate research program. Full understanding of hydrates and its physico-chemical and biogeochemical dynamics and phase stability can only be achieved through knowledge of the material properties of gas hydrate and its effects on the marine sediment in which it forms. Personnel from other disciplines and Divisions within NRL (Code 7000), particularly the Oceanography and Acoustics Divisions, should also be able to make substantial contributions.

The Workshop

To facilitate the process of developing a gas hydrate program, a workshop has held on 23-24 September, 1997 at NRL as part of an effort to identify major S&T issues, NRL research attributes and personnel who could best implement the enhanced gas hydrate research, and to identify particular field expertise and technology that could be brought to bear (Appendix 2). Although NRL personnel have been involved in marine research bearing on gas hydrates, particularly B. Hurdle, M. Max, P. Vogt, K. Crane, J. Gettrust, W. Wood, M. Rowe amongst others, it was felt that a workshop with the participation of external research experts would be valuable in developing the program. Therefore, a number of Non-NRL scientists with ancillary hydrate expertise were invited to attend the workshop (Appendix 3). Dr. B. Haq, NSF, and Dr. H. Guthrie, DOE, FETC, Morgantown, attended and contributed. In addition, three observers who are active in the Indian

National Gas Hydrate research program, I.L. Budhiraja, Gas Authority of India Ltd (GAIL); S.A. Vasant, KDM Inst Petroleum Exploration India, and M. Veerayya, National Institute of Oceanography India, were invited to attend because of their experience in recently initiating a national level gas hydrate research program in India and their stated interest to work with NRL. During the course of the meeting a draft Memorandum of Understanding (MOU) for joint research between GAIL and NRL was written.

The workshop was focused on the development of gas hydrate research at NRL which would have both scientific and practical components. The thrust of developing an integrated, multi-Divisional, and multi-institutional hydrate research program was to identify and access new sources of non-Navy funding for products and science consistent with Navy objectives and policy. To this end, we have defined a small number of first order integrated topics which meets the priorities of several funding agencies while producing significant scientific results. It must be noted that, while the workshop emphasized hydrates as Science and Technology (S&T) issues, it also considered potential technical payoffs and practical products. Our S&T thrust recognizes that in the emerging field of gas hydrate research, combined approaches are necessary, and simultaneous work at different levels of scientific and developmental endeavor are essential to telescope or shorten the time element in implementing a successful program.

The September workshop consisted of two main activities. In the first instance, a series of individual presentations were made that presented various scientific, engineering, and practical aspects of gas hydrates, so that the participants would have an information common reference platform for further considerations. The intent was to determine the "State-of-the-Art" in contemporary hydrate research. Discussion was encouraged throughout. The second, and most important, part of the meeting consisted of separating the participants into two working groups. One workgroup considered mainly marine science activities relevant to hydrate research including scientific observation and experimentation in the natural environment. The other workgroup focused largely on the materials and chemical aspects of hydrate, including laboratory-based science. Workgroup leaders afterward presented their preliminary results, which were open to general discussion, and which guided assembly of this document.

The workshop objectives thus progressed from discussions about the scientific state-of-the-art merits and issues, to more general concerns. The topics that the meeting was asked to consider were:

1. To demonstrate NRL potential for hydrate research
2. To outline an NRL hydrate research program utilizing its in-house resources
3. To consider possible expansion of NRL research activities and capabilities
4. To identify joint research activities and agencies/institutions
5. To identify potential funding sources

Summary of workshop topics

1. NRL potential for hydrate research

NRL scientists demonstrated their current research activities and presented results from their research (Appendix 2). These included:

1. High resolution multichannel seismic data acquisition and analysis, including

results from the Navy deep-tow, high-resolution multichannel seismic system.

2. Regional and detailed acoustic and optical image acquisition and analysis of the seafloor.
 3. Seafloor sampling of hydrate.
 4. Heat flow measurements in the vicinity of seafloor hydrates.
 5. Modeling of the geoacoustic affect of hydrates on low frequency acoustic propagation.
 6. Modeling of the geotechnical and physical property aspects of hydrate formation in marine sediments.

2. Existing NRL expertise and resources

Resources and expertise consist of two types, namely those already utilized and those available for addressing hydrate concerns. Those resources already employed include the NRL Code 7000 high resolution deep tow seismic system, and seafloor imaging and modeling capabilities, along with geological and geophysical modeling of the subsurface. However, a wide variety of modern analytical equipment and expertise, which to date has not been applied in gas hydrate studies, is available within Code 6000, especially within the Chemistry Division, Code 6100. A preliminary assessment of scientists and the first-order research areas in which it is felt that they can make near-term contributions is presented here, and further developments are not only likely, but to be encouraged.

Code 7400, Marine Geosciences Division

This Division holds virtually all the NRL personnel who have pursued gas hydrate research to date. Their work has been focused on the marine environment and many of their results and the technologies implemented are regarded as innovative. This existing expertise is an excellent platform on which to build both a continuation or expansion and the field studies, and a laboratory-based research program.

High-resolution reflection seismics and sidescan sonar seafloor acoustic imagery are part of the existing NRL sea-going capabilities, along with seafloor sampling and direct observations. Both of these techniques should be applied together allow for resolution of hydrate-related phenomena on and below the seafloor.

Multi-channel reflection seismic data of both near sea surface and near seafloor acquisition are the primary means by which the presence and disposition of gas hydrates and related gas deposits in marine sediments are known. NRL has been a major innovator in developing high resolution reflection seismic technology with its deep-tow apparatus developments and capability pioneered by NRL Code 7432. Although this capability may shortly not be unique, as its advantages over conventional surface-tow multichannel seismics for gas hydrate research are concerned, NRL houses a substantial body of expertise and experience in design and application of the technology, which is capable of further improvement. There is a major thrust to develop more accurate means to quantify the acoustic information to allow determination of hydrate volumes and disposition on the small scale, which it is hoped will lead to economic exploitation of the resource.

In addition, acoustic imagery acquisition and analysis of the seafloor, generated

from either multibeam bathymetric systems or towed sidescan sonar systems, is a representation of the intensity and travel time of received or backscattered acoustic energy. These acoustic intensities are dependent on the scattering strength of the seafloor, distributions of scatterers (e.g., hydrates), degree of bottom penetration, sub-bottom volume scattering, water column characteristics and insonification angle. Acoustic imagery and its interpretation with respect to the gas hydrate conservation cycle and methane flux from the seafloor, provides a potentially valuable tool for evaluation of the presence and character of seafloor gas hydrate. Acoustic imagery also can be used to link 2-D seismic data lines and aid overall evaluation of gas hydrate and gas in ocean seafloors.

However, focused research is needed to identify the precise backscatter effect associated with gas passage through seafloor. Most acoustic imagery experience to date has been gained in shallow water areas where there is neither sub-seafloor hydrate nor seafloor hydrate. NRL Code 7420 has a cadre of personnel, experienced in the acquisition and interpretation of deep ocean seafloor acoustic data, and is well placed to develop analytical techniques specific to the identification and characterization of oceanic gas hydrate.

Development of seafloor acoustic imagery as part of an NRL basic research program should consist of two parts; 1. Laboratory development of methodology and techniques, and 2. Field acquisition of selected sites in combination with other NRL field data acquisition. Some relevant acoustic imagery expertise already exists in 7420, which provides the capability to characterize large areas from the seafloor down to some depth below possible gas zones that may occur beneath the HSZ where the effects of the hydrate cycle have been obliterated by sediment compaction and fluid flow. Ocean floor targets for high resolution studies need to be selected from wide-area studies. Seafloor information may also allow the orientation and location of reflection seismic lines to be sited for optimum resolution of sub-seafloor features relevant to the study of hydrates.

A 3-D characterization of a seafloor and sub-seafloor area in which gas hydrate occurs will best show disposition of hydrate and gas, and structures in the gas hydrate economic zone and in sediments below. This differentiation is particularly relevant to assessments for economic target selection, in which more detailed geophysics, modeling, and definition of drilling targets and characteristics are the primary economic objectives. Seismic sections can be best tied with a complete, suitably resolved side-scan acoustic image of the seafloor. The seafloor imagery contains information about seafloor stability, fluid movement, and in the case of structures reaching the seafloor, the trace of these structures themselves. Although multibeam bathymetric mapping of hydrate study areas will resolve the bathymetry better than the bathymetry resolved as a by-product of the side-scan sonar survey, its extra resolution may not be useful without complimentary seafloor imagery.

One of the primary issues for gas hydrate research is the use and interpretation of acoustic energy to determine the disposition and volume of gas hydrate and gas in oceanic marine sediments. A number of different geophysical models have been proposed, but to date they are very general and not closely based on detailed geological processes, especially for mature hydrate deposits. It is important to carry out modeling with respect

to both biological and geological processes, so that realistic geophysical and numerical models can be established and tested. Modeling of the hydrate- and gas-rich sediment has been carried out and published along with geological process modeling of seafloors having gas hydrate and has been working with geophysicists carrying out numerical modeling. Continuation of these modeling efforts should be part of any broad NRL basic research program concerned with oceanic hydrates. It is anticipated that this modeling will be strongly iterative for the NRL geophysical researchers.

The approach to the modeling is a combination of applying knowledge of the geological history of both sedimentation and hydrate formation with a view to how this affects the geotechnical and geophysical aspects of hydrate formation and dissociation. The work is both qualitative and quantitative, and has led to a number of publications. Continuation of these modeling efforts as basic research should be part of any broad NRL research program concerned with oceanic hydrates. It is anticipated that this modeling will be strongly iterative with geophysicists with access to refined seismic data.

With a more detailed understanding of the distribution of hydrate and associated gas deposits, a more realistic assessment of the basic process of marine sedimentation and hydrate formation and diagenesis can be made. The simple Hamiltonian model for marine sedimentation is inappropriate for marine sediments containing hydrates. As hydrates occur very widely and the conditions for their formation likely operated through most of geological time, a new model is necessary. In addition, more precise calculations of the affect of the oceanic hydrate system can be made with respect to global atmospheric greenhouse and climate.

Near-term Navy relevance to better geological modeling of the hydrate system is twofold: a. Improved understanding of seafloor stability, which has a direct impact upon any bottom-mounted systems or engineering artifacts, and 2. Better geoacoustic models that are vital for understanding the affect of the hydrate system on low frequency acoustic propagation. Among future issues are: Energy security, methane as the primary feedstock for a Navy fuel, potential at-sea fueling systems, in-situ, fixed site energy sources, ocean carbon cycling, etc.

3. Expansion of NRL research capabilities

Topics that should be considered in a broad hydrate research program (Appendix 4) clearly span a number of Divisions and Branches. Individual Division programs may in themselves be quite detailed (Appendix 5). A number of issue areas have been identified:

Code 5500, Information Technology Division

1. Advanced electronic display and visualization techniques under development could substantially alter the accessibility of the visual information gained from 3-D display of compiled geophysical data, interpretive data sets such as methane volume quantification, and extractive modeling.

Code 6100, Chemistry Division:

1. Ocean carbon cycling, methane flux and generation studies.

2. Development of real-time, in-situ gas (especially methane) sensors. The gas sensors will monitor various specific gases dissolved in the water, and present in the sediment. Multiple approaches should be pursued to ensure success, and to operate under various conditions.
3. Isotope studies of hydrate-derived gases, organic matter and microbiological community to assess sources of fixed carbon.
4. Production and laboratory study of synthetic hydrates to highlight hydrate formation dynamics/stability/lattice occupancy issues. Proton NMR will be used to quantitate methane in the sediment, and to provide spatial imaging of the hydrate distribution.

Code 6600 Condensed Matter and Radiation Sciences Division

1. Micro-Electronic Mechanical Systems (MEMS) for exploration and recovery of marine gas hydrate deposits. Assess and report on MEMS technology suitable for monitoring physical conditions in hydrate-gas rich seafloor.
2. X-Ray diffraction studies of phase equilibria in gas hydrate systems. Laboratory measurements of the structure and kinetics for naturally occurring methane hydrate systems in order to obtain the best paradigm for methane recovery using depressurization. Raman studies will also be used to characterize the structure of hydrates in the laboratory.
3. Trace element and isotopic analysis of naturally occurring gas hydrates. Determine elemental constituents of natural sediments and hydrates at levels below parts per million, and the isotopic make-up of these materials to levels below parts per trillion. Analyze isotope data to learn chronology of hydrate formation, historical extent of hydrate stability zone, and possibly the Paleological temperature of the area.
4. Theoretical and computational structure and dynamics of gas hydrate systems. Determine of the electronic and phonic structures and the kinetics of hydrate reactions and calculations and predictions of the reaction of these materials with marine sediments. This effort will provide broad technical assistance for other activities.

Code 6700, Plasma Physics Division

1. Hyperspectrometer development and application for study of in-situ methane flux in the oceans.

Code 7100, Acoustics Division:

1. Application of full field inversion techniques for seismo-acoustic properties relevant to the HSZ.
2. Identification of the best frequencies and acoustic parameters for seismo-acoustic study of hydrates. Optimization of existing seismic equipment. Design of new, hydrate-specific seismic equipment.

Code 7400, Marine Sciences Division:

1. Area analysis and economic and scientific target identification using optimized seismic and image analysis techniques optimized for hydrate research.

2. Geological and geophysical modeling integrating acoustic and electrical data technique development and analysis.
3. Detailed seafloor studies of geologically unstable areas using a wide variety of geophysical equipment, direct sampling and observation, and in-situ experimentation.

A number of draft proposals detailing activity within these areas have been prepared as part of a unified response to the suggested program outline.

4. Joint Research activities and agencies/Institutions

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5. Potential funding sources

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Recommendations

1. A small group of Code 7000 and 6000 scientists should be named who can coordinate development of the combined Gas Hydrate Research Program (CGHRP). A group leader should be named.
2. Work with potential funders to develop proposals with near-term starts.
3. Initiate activities as rapidly as possible.
4. Consider further program development.

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Part 2. Oceanic gas hydrate: Workgroup summaries and presentations.

Work Group 1: Marine Sciences

P. Brewer

Summary

The working group on gas hydrates and Marine Sciences recognized that there were both Navy, and broad marine science, issues that should be addressed in any research effort.

Key questions identified by the group are:

- 1) The enormous size of the marine hydrate reservoir, and necessary assessments of its regional magnitude and distribution. Key geopolitical and environmental threat arguments rest on this data.
- 2) The role of gas hydrates in global change and the possibility of hydrate destabilization as a result of global warming in the next few years.
- 3) The possibility of sub-sea slope failure in critical regions as a result of hydrate instability.

The tools necessary for scientists to tackle these problems are:

- 1) Advances in sea floor, and sub-sea floor, imaging. NRL has specific skills and expertise in this area.
- 2) Geochemical correlations with acoustic imagery. The external academic and national laboratory community has the needed skills in this area.
- 3) The need for new, high resolution, sub-sea floor imaging tools so as to bridge the scale gap between acoustic and chemical detection strategies.
- 4) Advances in-situ chemical sampling and detection protocols and strategies so as to provide samples to support realistic assessments.
5. Understanding the biogeochemical processes which affect methane hydrate formation and stability.

Unsolved problems relate to:

- 1) The relationship between fluid flow in sediments and hydrate structure and formation, and the time scale of hydrate generation.
- 2) The determination of gas concentrations and distributions in-situ, especially near the sediment-water interface.
- 3) How to provide specific assessments of the potential for instability at critical sites.
- 4) How to couple geophysical fluid dynamic models with the chemistry of hydrate formation and dissociation.
- 5) How to provide predictive assessments of these topics so that models and concepts may be tested.

Recommendations from the group include:

- 1) The development of new and enhanced sub-sea floor seismic imaging tools of finer scale resolution.
- 2) The development of enhanced chemical sampling and detection systems capable of matching and verifying the acoustic information.
- 3) The selection of a limited number of well defined and surveyed sites for comprehensive study that may serve as test beds for technique and model development, for detailed sampling, and where monitoring stations may be closely integrated with the rapidly evolving global change signals.

Discussion

The size of the gas hydrate reservoir, which exists almost entirely in shallowly buried, moderate to deep marine sediments, has been estimated as about 10,000 Gigatons of carbon (10~9 grams carbon), or about twice the amount of carbon contained in all other fossil fuel sources (coal, oil, gas) combined. A great deal of uncertainty surrounds this number, which is based largely on seismic reflection data combined with drilling at a few sites. Both the refinement of this estimate, and the identification of the manner in which the material is distributed i.e. where large concentrations rather than dispersed material occurs, are basic needs and concerns of several government agencies, and also reflect the identification of sites around the world where nations may be expected to critical interest in the years ahead. Recent evidence presented at the meeting suggests that for the US EEZ the earlier estimates of the total hydrate abundance may be too low. The problem of correlating acoustic signatures with direct geochemical evidence of hydrates is crucial. Present seismic imaging techniques typically can not resolve structures on a small enough scale to be well correlated with the point source geochemical information.

There is concern that the process of global warming now established in the atmosphere, and most likely affecting the ocean, could cause release of large amounts of gas now trapped in the hydrate form in marine sediments. The release of gas could exacerbate the already large methane build up, would represent the loss of a potential resource, and could cause severe local instabilities in the affected regions. Although this problem was first identified about 1982, and has since been widely discussed, there has been little progress in quantifying the argument. The separation of the geological community concerned with hydrates, and the oceanographic community concerned with global warming and biogeochemical cycles, has contributed to this. Evidence presented at the workshop showed that the penetration of 20th century chemical tracers into deep deep oceanic water has now reached depths at which gas hydrates are known to occur. Key to evaluate the impact of ocean warming and methane flux from production in the marine sediments through the ocean to the atmosphere is biological assimilation relative to atmospheric transport. We need to establish protocols for the detection and prediction of temperature changes, and their geochemical consequences, at critical sites.

Gas hydrates occur on continental slopes, and the gas accumulations, and changes in sediment properties caused by the presence of hydrates create regions of weakness that

can cause massive undersea slope failure. The relationship between sediment mass-flows, and other sediment failures, seems well established by field evidence. We understand little of the processes by which catastrophic failure can occur, yet as nations seek to explore the hydrate resource, and as global warming occurs, the need for such understanding is fast becoming critical.

The primary exploration and site identification tool or technology is the use of seismic imaging. It is impossible to proceed without the use of this resource. NRL expertise in high frequency geophysics (DTAGS), and sonar mapping can be exploited with enormous benefit in the delineation and identification of the small geologic features caused by fluid flow. The 2-3 meter scale resolution anticipated from DTAGS allows unprecedented resolution of the Bottom Simulating Reflector (BSR). The detailed reflection amplitude anomalies associated with gas and hydrates may also delineated at this fine scale. NRL expertise in side scan sonar can also be exploited for hydrate research. Fluid flow mechanisms which may serve to concentrate the hydrate also serve as a conduit for venting gas and forming hydrate on the exposed sea floor. The features thus created may be detectable by side scan sonar, which can be conducted on a broad scale. Other new and promising technologies include NRL-DC chirp sonar, and 1-D algorithms to provide inverse solutions for the porosity and sound speed structure of the upper 50m of sediments. There is the possibility of 3-D tomographic inversion experiments for resolving the structure of a few km-square area with several hundred meter depth penetration. We are encouraged by plans for the development of a new swath Subbottom System with a parametric low frequency source by NRL. This capability will permit the identification of critical shallow subsurface features, such as faults, and other fluid flow conduits. One attractive feature is the potential for operating this system in the same mode as a side scan sonar, thus providing large areal coverage. Advances in Remotely Operated Vehicles (ROV) technology, driven by both oil field and military needs, have made the field manipulation of hydrate systems, unstable at surface temperature and pressure, possible. This developing technology opens up new and exciting opportunities for scientific study.

Acoustic imagery of gas and hydrate systems remains sterile without geochemical verification. Gas hydrates are just one component of the marine interstitial gas reservoir. Significant amounts of gas also occur dissolved in pore waters, and as free gas bubbles. We know very little about the amounts, distributions, and mobility of these gas species, especially in areas away from commercial hydrocarbon exploration sites; however establishing total gas concentration profiles is critical for understanding the origins and dynamics of the gas hydrate deposits. The principal tools and skills required here typically reside within NRL, and also within the academic, commercial, and other government laboratories. The development of pressurized samplers for return of valid, stable specimens to surface laboratories is one essential need. The invention of new trace component, and isotopic, tools to explore the age and chemical dynamics of hydrate systems will be required. Modern in-situ sampling and analytical technologies now being developed show great promise here. Self contained miniature detection systems employing micro-electronic mechanical systems (MEMS) are now under development, and may be carried by submersibles and ROVs. Enhanced chemical detection strategies also permit

smaller sample size, and greater return on payload for sampling opportunities. We strongly encourage these developments.

There are many unsolved problems in this area. One critical aspect is the relationship between fluid flow in sediments, and hydrate structure. Hydrates occur in many forms: as large nodules, as sheets or layers, or as finely dispersed material. We have only preliminary notions of how to explain these distributions, and even less knowledge of how to predict it from seismic imaging. The age and mobility of hydrate masses is comparably unknown. Also, the determination of gas concentrations in-situ remains a hard problem, but one that is addressable.

We do not have direct ways to assess the possibility of hydrate instability at specific sites, either due to the advancing wave of global warming, or the possibility of earthquake destabilization. It appears quite possible to place the dissociation of gas hydrates within the context of global warming today, but strategies to do so need to be formalized and implemented.

Models of the geophysical fluid dynamics of flow in porous media need to be coupled with the unique characteristics of hydrate formation: brine rejection, expansion cooling, release of heat on formation, and the net buoyancy of the hydrates within the sediment matrix. Finally, the use of models for predictive assessments at key sites, and the testing of these ideas and predictions against real data, needs to be accomplished.

Workgroup 2: Material Properties and Chemistry of Gas Hydrates

D. Nagel

NRL has demonstrated capability in gas hydrate R&D in the areas of both the field and the laboratory. The marine science program has studied hydrates in the western Pacific (Nankai Trough area), eastern Pacific (Canadian and northern U.S. Pacific margins), Svalbard margin of the Nordic Sea, Blake Ridge and basin area of the U.S. east coast margin, and used these data to address the general modeling of the geological aspects of hydrates. Several experimental or laboratory capabilities suitable for research into the physical and chemical aspects of hydrate exist, but have only been employed to date by NRL in studying non-water based hydrates.

Laboratory work examining many naturally occurring materials is commonly carried out by producing laboratory analogues to the naturally occurring materials, so that knowledge of their character and properties can be measured and extrapolated to natural substances (e.g., hydrates). In order to understand the response of hydrates in both formation and dissolution, their characteristics and properties, which are dependent on its molecular structures and composition, must first be understood. As for other naturally occurring materials, e.g., granite formed from high temperature silicate minerals, understanding of the behavior of feedstock reagents to the changing pressure-temperature conditions that cause their formation is vital to understanding the impact of such suites of variables.

Naturally occurring hydrates that have formed within the sea water-sediment system are accessible easily only at the seafloor. A number of sites, which could be termed 'Natural Laboratories' are known (northern Gulf of Mexico, Svalbard margin, Black Sea, etc.) and can be sampled using existing technology, which needs to be optimized for pressurized hydrate recovery. The pressure-temperature and chemical conditions of seafloor sites can be replicated in the laboratory, and comparison of naturally occurring and laboratory samples can be used to provide a relatively inexpensive check of the analogous formation process. Study of hydrates forming within sediment is important because of the possible catalytic affects of sediments, which are bound to affect local chemical environments (e.g. sediment constituents).

Although hydrates form easily in the water column, and a number of recent field experiments have fabricated hydrates of both CH₄ and CO₂ in this way, hydrates that may occur naturally in the water column float upwards because of their buoyancy and dissociate in the lower pressure and higher temperature regime of shallower water. Comparison between hydrate fabricated in the laboratory and the 'in-situ' laboratory of the ambient deeper-sea pressure-temperature conditions, offer the possibility of direct comparison. In contrast, hydrates forming in the water column are of no economic or other interest in themselves, because they change to gaseous methane as they drift upwards except in very special cases. However, study of hydrate formation within sea water does offer opportunities for the study of methane gas flux to surface waters that might otherwise become dissolved within seawater and dispersed by currents. In fact, the recognition that hydrates are only quasi-stable in the water column has previously been

used to argue against their study. There is essentially nothing known about the chemistry and kinetics of such mid-water processes. This is an area that has been overlooked by the hydrate research community to date, but one in which NRL can bring capable personnel and extensive equipment to bear.

The major hydrate environment sediments, and the only one of interest for energy issues, is not as amenable to laboratory comparison. Certain information, such as the age distribution of hydrate within a mature oceanic hydrate, can only be derived from in-situ sampling. But more general information about hydrate material and chemical properties must be revealed by the study of sub-seabed analog hydrate+sediment analogs. Hydrates within the seafloor can only be accessed by drilling, which is a costly practice. The Ocean Drilling Program is likely to remain the best source of deep samples. Developing research relationships with companies may also generate in-situ samples. Because hydrate stability and thermodynamics near the base of the hydrate is of the greatest importance for commercial development of hydrates, it is likely that most of the thermodynamic and chemical issues related to hydrate-gas-water reactions at those seafloor depths will be studied by using laboratory analogues. These experiments will be only rarely checked against actual samples.

In addition to samples recovered by remote drilling, it is possible to gather targeted samples by direct intervention, via diving, at hydrate fields that are known to occur on the seafloor. Diving using manned submersibles and with ROVs has been undertaken to examine and sample seafloor hydrates for over 10 years. Dives are usually located using earlier geophysical surveys that have identified likely seafloor locations for hydrate. The actual field time on station for a full dive-sampling program is much less than for drilling; the transit times are usually the greater part of the daily cost charge. If possible, outcrops of hydrate are identified and then visited for observation, measurement, and sampling.

NRL can take part both in the field, in the laboratory, and in the design and implementation of new instrumentation. The inherently integrated study of hydrate through observation, theory, and calculations applies principally in the areas of phase stability and kinetics. Conversely, modeling and simulation, which are both essentially laboratory approaches, will strongly guide the development of both laboratory and field programs. Success in modeling and simulation requires the acquisition of large amounts of data both from in-situ and synthetic hydrates. These data provide a only as foundation for developing new data gathering technologies, key aspects of which are now only known in outline.

1. Laboratory

A first approach based on the natural environment indicates laboratory work should try to use analogues of the dirty systems found in the natural environment. Such dirty systems would include quantities of naturally occurring sediment and sea water constituents, and trace gases mixed with the methane carrier. In addition, it will be important to work with models of the natural environment to ensure that the attributes actually driving the system are those that are initially and best studied. Development of a hydrate research program must ensure that time and resources are not squandered

exploring hydrate related research dead-ends. Hydrate has proven kinetically very easy to nucleate and grow from gas and methane in the ocean environment, but laboratory analogues often form the hydrate in ways that are not found in nature, for instance beginning with crushed ice. It is questionable whether unnatural nucleation and growth modes will yield the acceptable analogues for natural growth states of methane hydrate.

Significant concerns:

- Experimental design for artificial hydrate formation to model natural hydrates
- Replicate Experiments
- Characterize material from both the natural environment and field
- Structure and crystal morphology, crystal zoning, element and molecule partitioning, affect of additional molecules on structure and thermodynamics
- Sample preparation and preservation
- Correct time scales for hydrate formation
- Thin films as end products or nucleation regions
- Gel growth matrices

2. Field Studies

Hydrates provide a focus for design of new measurement instrumentation:

- a. Sensitive, real-time, georeferenced underwater methane detector
- b. Micro CCD for studying crystal morphology and grain boundary effects in sediments
- c. In-situ microscopy and/or spectroscopy
- d. Specialized equipment for ROV measurement and sampling

Help develop a high pressure retrieval system for seafloor and core samples

Carry out seafloor and water column experiments as true analogs for in-situ conditions

Identify suitable hydrate tracers such as heat flow or bioproducts of methane consumption

Geomicrobiology below the HSZ, wherein the major part of the gas is produced, and in the upper part of the HSZ, where methane may be consumed, are important factors in the overall methane flux

Samples from ambient conditions produced by drilling. Characterization, measurement, and examination as external reference data for comparison with experiments

- a. Hole and core logging
- b. Samples
- c. Full geochemistry
- d. Continuous core if possible

In-situ methane flux studies.

3. Mixed System Concerns

- a. Systematic study in the laboratory of $\text{CH}_4 + \text{H}_2\text{O}$, other than pure molecular H_2O , will naturally involve other materials, principally the potential sedimentary materials.

- b. Micro responses and their relation to macro morphology
- c. Structural kinetics
- d. Structural interaction with 3rd surfaces (of both other hydrate of similar and related crystal structure and with all sediment materials - tectosilicate and phyllosilicate)
- e. Devise methods of isotopically dating hydrates in order to understand crystallization and fluid movements within HSZ
- f. Nucleation, growth, autocatalytic effect, first and second nucleation barriers, type of growth, etc.
- g. Development of biomarkers to study chemical paths for carbon and other elements relevant to the oceanic hydrate system

4. Technology Gaps: Develop and Implement In-Situ Instrumentation

There is a clear need for:

- a. In-situ, long duration probes for monitoring methane gas and hydrate in the oceanic water column
- b. New deep-tow survey systems are necessary that will yield areal acoustic, image, and chemical coverage
- c. In-situ optical monitoring and observation and measurement systems for sedimentary hydrate
- d. Dissolved methane sensing systems for long-term deployment in-situ
- e. Specialized multichannel seismic systems designed specifically for maximum performance in the hydrate economic zone
- f. Specialized heat flow apparatus
- g. Fiber optic probes to examine seafloor hydrates
- h. NMR applications. The techniques of solid-state Nuclear Magnetic Resonance (NMR) spectroscopy can be used to characterize both naturally-occurring and laboratory samples of methane and mixed water hydrates. Structural information relating to cage occupancies and the effects of mixed gases, and kinetic questions relating to formation and dissolution, can be addressed. The molecular dynamics of the 'caged' molecules can be distinguished in the search for additional "signatures" relating to complex structural details. In addition, low magnetic field investigations may also be used to explore the feasibility of hydrate-optimized NMR core logging in a drill hole.
- i. Raman spectroscopy for high resolution chemical analysis underwater
- j. Economic high pressure laboratory facility for dealing with pressurized hydrate samples recovered from the HSZ

Summary and current situation of knowledge about hydrate chemistry and thermodynamics

Although the phase stability and stability of methane hydrates with respect to a limited number of other associated gases is reasonably well known, the kinetics of formation, growth, and dissociation are not well known for the base-of-hydrate of

interest for economic exploitation. Most of the research into hydrate chemistry and thermodynamics, for instance, has been done by the hydrocarbon industry with a view to inhibiting growth of hydrates. This is because hydrate can commonly form in pipelines and risers, and can clog them, severely inhibiting gas flow. This research has produced a body of knowledge on the chemical and physical chemical behavior that is clearly skewed with respect to the many other topics and natural environments, especially those that exist at the base of oceanic hydrates. The new focus of potential funding agencies is understanding those attributes of the physical-chemical and geological (geotechnical) situation existing in the region from which methane is potentially to be extracted.

The role of NRL in Gas Hydrate R&D is conditioned by the necessity to choose a course that will best fit opportunities. Execution of a program to address these opportunities depend largely on the existence and use of new funding sources from outside the Navy. Development of a program will thus depend on knowing what use the end-user is going to make of the information. It is important to ensure that NRL develops an integrated work program that takes into account Navy issues and needs, and addresses sponsor concerns.

The logistical and political access to oceans by the Navy and NRL, either working entirely with other US research interests or in concert with foreign research interests, can be expected to enhance NRL's position as an active sea-going participant in a wider US research program, and world-wide. NRL and the Navy already have memorandum of understanding with a number of other nations and research bodies, as well as a history of joint work on both the national and international level. NRL should also take the initiative in organizing joint research with both research institutions and National Laboratories and fully bring the Navy technology and expertise into the development of joint research programs.

Hydrate In Marine Sediments

W.P. Dillon & M.D. Max

What is it? Where is it?

Gas hydrate is a methane-bearing, ice-like crystalline substance that occurs in abundance in marine sediments and stores immense amounts of methane, with major implications for energy resources and climate. Furthermore, gas hydrate influences the physical properties of sedimentary deposits. Gas hydrate is a crystalline solid; its building blocks consist of a gas molecule surrounded by a cage of water molecules. Gas hydrate looks like ice, and is very similar to ice, except that the crystal structure is stabilized by the guest gas molecule, which is normally methane. Gas hydrate is stable at moderately high pressure and low temperature and exists within ocean floor sediments at water depths greater than about 500 m (shallower in the Arctic). The zone in which hydrate is stable in the sediments extends from the sea floor, commonly to hundreds to as much as a thousand meters below the sea bottom.

How much?

Gas hydrate is a concentrator of methane (one unit volume of gas hydrate can contain >160 volumes of gas at Standard Temperature and Pressure [STP]) and energy densities in reservoirs are high. The worldwide amount of methane carbon in gas hydrate is considered to be equivalent to about twice the amount of carbon that resides in all fossil fuels on Earth (including coal), and it represents an amount of methane that is, perhaps, 3000 times the amount in the present atmosphere.

Why is it important?

Gas hydrate is important primarily because it contains huge amounts of methane in a concentrated form and because it influences the physical properties of sedimentary deposits, particularly strength and acoustic velocity. However, the natural controls on hydrate and hydrate's impact on the environment are very poorly understood. Three main issues are:

- 1. Hydrocarbon resources** - Extraction of gas from hydrates could provide a very large energy and fixed-carbon feedstock resource, and additional gas supplies appear to be trapped beneath the hydrate layer in ocean sediments. Extracting methane from the marine gas hydrate for use as an energy resource will present engineering problems, but access to the hydrate is easy because it exists in the upper hundreds of meters of ocean floor sediments. The presence of an existing distribution and utilization system is a further advantage.

Methane as a fuel is relatively less-polluting than other hydrocarbons because methane has a higher hydrogen/carbon ratio, and so produces a minimum of carbon dioxide. Further, methane combustion evolves no other pollutants such as particulate matter or sulfur compounds. Speculative scenarios for the distant future might include emplacement of fuel cells on the sea floor to use hydrate-derived methane as an energy source to generate hydrogen, which could be piped ashore to support a nonpolluting, hydrogen-based energy distribution system. The waste carbon dioxide might be disposed of

as a sea-bottom gas hydrate (carbon dioxide also forms gas hydrate at seafloor conditions). Hydrate methane would also be used as the raw material to be dissociated to extract hydrogen, as it requires only 15% as much energy to extract a mole of hydrogen from methane compared to water as a hydrogen source.

The use of methane from hydrate as an energy and feedstock source could result in much differently arranged energy and petroleum resources in the world. Methane hydrate concentrations can occur in areas where other energy resources are poor, but where energy demand is high because of high population density (as is common in coastal areas). The South Carolina/North Carolina area is an example in the U.S., where large deposits of hydrates occur offshore in the Blake Ridge. Any country with significant deep-water boundaries is likely to have hydrate deposits. This situation might significantly change the importance of Middle East petroleum. The geopolitical impact of, for example, discovery of large gas resources in Japan's or India's territorial waters would be extremely significant. Note that these two countries have embarked on exploration programs to evaluate their offshore gas hydrate resources.

2. Seafloor faulting and landslides - Gas hydrate is concentrated in the sediments of the continental margins. Small changes in temperature or pressures can cause breakdown of hydrate, thus substituting a much weaker material (gassy, watery sediment) for a stronger one in a thin layer within the sediment and probably generating gas pressures that would encourage landsliding. Many landslides on the U.S. Atlantic continental margin have occurred on low slopes that would be expected to be stable and landslide scars are concentrated at depths near the top of the range of hydrate stability (500-700 m). Thus, circumstantial evidence implicates hydrate processes affecting sediment slumping and collapse. Major sediment collapse features observed in USGS seismic profiles and sidescan sonar images are almost certainly related to gas hydrate breakdown. Such breakdown may have occurred when pressure at the sea floor was reduced by the lowering of sea level caused by the formation of polar ice caps.

Extraction of methane from hydrate will entail dissociating the hydrate to release the gas, with the possible hazard of triggering sediment mass movements. Therefore the strength of hydrate-bearing and gassy sediments and the changes associated with hydrate formation and breakdown need to be studied. An understanding of this is critical for safe and effective extraction of hydrate gas, and also for any use of the seafloor for petroleum extraction, defense, waste disposal, etc. Recent shallow gas escapes and sediment mobilization that disrupted deep-water exploration drilling in the Gulf of Mexico are likely to have been caused by gas trapped beneath a hydrate-cemented sealing layer.

3. Climate change - Methane is ten times more effective as a greenhouse gas than carbon dioxide. The release and absorption of large volumes of methane from seafloor hydrates may have had major impacts in modifying the Earth's climate. For example, global cooling would be expected to lead to ice cap expansion, which would tie up ocean water in vast continental ice sheets and thus lower sea level. Lowering of sea level would reduce pressure on seafloor hydrates, which would cause hydrate dissociation and gas release. This atmospheric methanewould increase the greenhouse effect, and cause global warming. Thus hydrate may be part of a great negative feedback mechanism leading to

stabilization of Earth temperatures.

4. The oceanic hydrate system, is closely associated with life-processes. Understanding the age distributions of the existing hydrate concentrations may strongly affect development of extraction strategies. Age distribution will shed light on growth and dissolution rates, as well on supply of reactants and fluid movements. Hydrate renewability, and the affect of removing methane from the natural oceanic hydrate system and world carbon cycle are at present almost completely unknown. Existing hydrates often cap and prevent the release of some subjacently derived methane. Some questions that require answering are: if a slope collapses, or the hydrate is commercially extracted, how quickly will stable hydrate reform? Will there be a sudden increase of methane release as the flow limitation of the cap is removed? Or does hydrate reform hydrate so quickly as to be of no consequence. The dynamics of hydrate growth within the sediment is an important question that will have an impact upon issues of global warming, acoustic property alteration of seawater, and the carbon cycle in the ocean.

Resource Potential of Marine and Permafrost Associated Gas Hydrates

T.S. Collett

Introduction

Recently completed industry and government funded research studies have significantly contributed to the growing interest in the energy resource potential of natural gas hydrates. The discovery of large gas hydrate accumulations on the North Slope of Alaska and off the southeastern coast of the United States have confirmed the possibility that gas hydrates may represent an important energy resource for the future. However, significant to potentially insurmountable technical issues need to be resolved before gas hydrates can be considered a viable energy resource option.

Gas hydrates are naturally occurring crystalline substances composed of water and gas, in which a solid water-lattice accommodates gas molecules in a cage-like structure, or clathrate. Gas hydrates are widespread in permafrost regions and beneath the sea in sediment of outer continental margins (Fig. 1). While methane, propane, and other gases can be included in the clathrate structure, methane hydrates appear to be the most common. The amount of methane sequestered in gas hydrates is enormous, but estimates of the amounts are speculative and range over three orders-of-magnitude from about 100,000 to 270,000,000 trillion cubic feet (adapted from Kvenvolden, 1993). It is likely that the amount of gas in the hydrate reservoirs of the world greatly exceeds the volume of known conventional gas reserves. However, relatively little work has been done to assess the availability and production potential of gas hydrates.

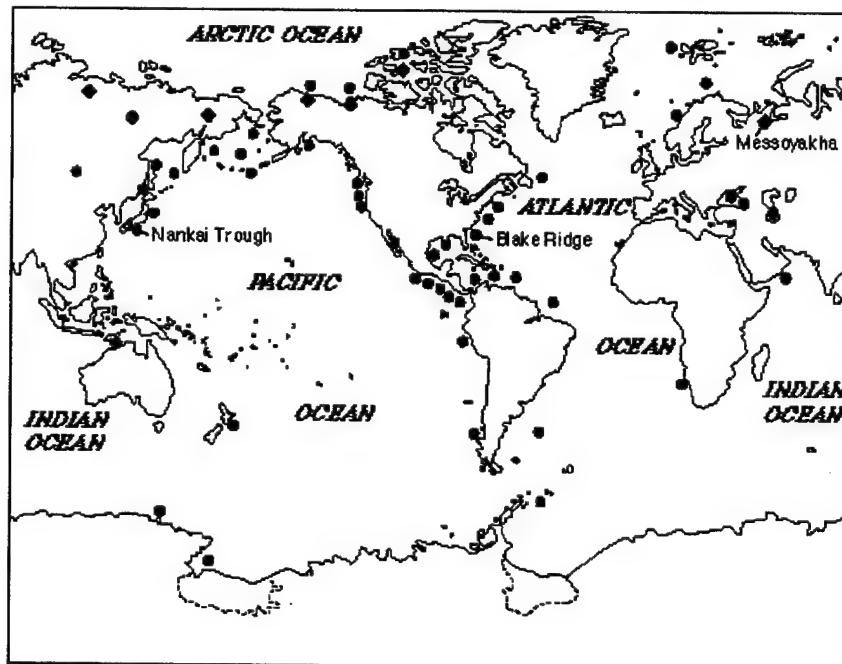


Figure 1. Location of known and inferred natural gas hydrate occurrences in the

World (modified from Kvenvolden, 1993).

The primary objectives of our gas hydrate research efforts at the U.S. Geological Survey are to document the geologic parameters that control the occurrence of gas hydrates and to assess the volume of natural gas stored within the gas hydrate accumulations of the United States. In this paper we discuss the results of our recently completed National assessment of natural gas hydrate resources and we attempt to evaluate the resource production potential of gas hydrates and examine the technology necessary to economically produce gas hydrates. This paper ends with a overview of the plans for production from gas hydrates in Japan and India.

Gas Hydrate Technical Review

Under appropriate conditions of temperature and pressure (Fig. 2), gas hydrates usually form one of two basic crystal structures known as Structure I and Structure II. Each unit cell of Structure I gas hydrate consists of 46 water molecules that form two small dodecahedral voids and six large tetradecahedral voids. Structure I gas hydrates can only hold small gas molecules such as methane and ethane, with molecular diameters not exceeding 5.2 angstroms. The unit cell of Structure II gas hydrate consists of 16 small dodecahedral and 8 large hexakaidecahedral voids formed by 136 water molecules. Structure II gas hydrates may contain gases with molecular dimensions in the range of 5.9 to 6.9 angstroms, such as propane and isobutane. At conditions of standard temperature and pressure (STP), one volume of saturated methane hydrate (Structure I) will contain as much as 164 volumes of methane gas - because of this large gas-storage capacity, gas hydrates are thought to represent an important source of natural gas.

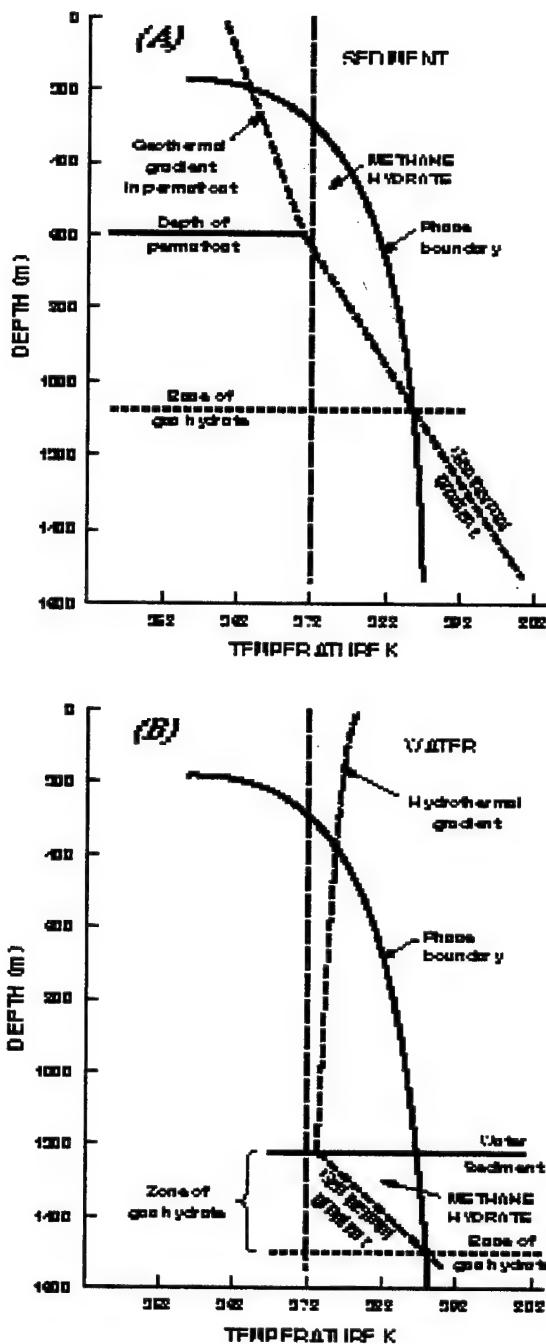


Figure 2. Arbitrary examples of different depth-temperature zones in which gas hydrates are stable: A, a permafrost region; and B, an outer continental margin setting (Sloan, 1990).

On a macroscopic level, many of the gas hydrate mechanical properties resemble those of

ice, because hydrates contain a minimum of 85 percent water on a molecular basis. Of interest are the phase-equilibrium properties of gas hydrates, which are mostly controlled by the fit of the guest gas molecules within the hydrate water cages. For example, the addition of propane to a pure methane hydrate changes the hydrate structure (Structure I >> Structure II) and broadens the conditions in which the hydrates can occur. For a complete description of the structure and properties of hydrates see the summary by Sloan (1990).

Permafrost Gas Hydrates

Onshore gas hydrates are believed to be present in the West Siberian Basin and are believed to occur in other permafrost areas of northern Russia, including the Timan-Pechora province, the eastern Siberian Craton, and the northeastern Siberia and Kamchatka areas. Permafrost-associated gas hydrates are also present in the North American Arctic. Direct evidence for gas hydrates on the North Slope of Alaska comes from a core-test, and indirect evidence comes from drilling and open-hole industry well logs which suggest the presence of numerous gas hydrate layers in the area of the Prudhoe Bay and Kuparuk River oil fields (Collett, 1993). Well-log responses attributed to the presence of gas hydrates have been obtained in about one-fifth of the wells drilled in the Mackenzie Delta, and more than half of the wells in the Arctic Islands are inferred to contain gas hydrates. The combined information from Arctic gas-hydrate studies shows that, in permafrost regions, gas hydrates may exist at subsurface depths ranging from about 130 to 2,000 m.

Marine Gas Hydrates

The presence of gas hydrates in offshore continental margins has been inferred mainly from anomalous seismic reflectors that coincide with the predicted phase boundary at the base of the gas-hydrate stability zone. This reflector is commonly called a bottom-simulating reflector or BSR. BSRs have been mapped at depths below the sea floor ranging from about 100 to 1,100 m (Kvenvolden, 1993). Gas hydrates have been recovered in gravity cores within 10 m of the sea floor in sediment of the Gulf of Mexico, the offshore portion of the Eel River Basin of California, the Black Sea, the Caspian Sea, and the Sea of Okhotsk. Also, gas hydrates have been recovered at greater sub-bottom depths during research coring along the southeastern coast of the United States on the Blake Ridge, in the Gulf of Mexico, in the Cascadia Basin near Oregon, the Middle America Trench, offshore Peru, and on both the eastern and western margins of Japan.

Gas Hydrate Resource Assessment

Because gas hydrates are widespread in permafrost regions and in offshore marine sediments, they may be a potential energy resource. World estimates for the amount of natural gas in gas hydrate deposits range from 5.0×10^2 to 1.2×10^6 trillion cubic feet for permafrost areas and from 1.1×10^5 to 2.7×10^8 trillion cubic feet for oceanic sediments (adapted from Kvenvolden, 1993). The published gas hydrate resource estimates show considerable variation, but oceanic sediments seem to be a much greater resource of natural gas than continental sediments. Current estimates of the amount of methane in the world gas hydrate accumulations are in rough accord at about 7×10^5 trillion cubic feet.

A major goal of our resource appraisal work in the U.S. Geological Survey is to estimate the gas hydrate resources in the United States, both onshore and offshore. Similar to the assessment of the conventional resources in the 1995 U.S. Geological Survey Oil and Gas

Assessment (Gautier and others, 1995), this appraisal of gas hydrates is based on a play-analysis scheme, which was conducted on a province-by-province basis. We have defined, described, and assessed all the gas-hydrate plays in the United States regardless of their current economic or technological status. Therefore, this assessment is concerned with the in-place gas hydrate resources--that is, the amount of gas that may exist within the gas hydrates without reference to its recoverability. In a play analysis method, prospects (potential hydrocarbon accumulations) are grouped according to their geologic characteristics into plays. The geologic settings of the hydrocarbon occurrences in the play are then modeled. Probabilities are assigned to the geologic attributes of the model necessary for generation and accumulation of hydrocarbons. In this appraisal method, geologists make judgments about the geologic factors necessary for the formation of a hydrocarbon accumulation and quantitatively assess the geologic factors that determine its size.

In this assessment, 11 gas-hydrate plays were identified within four offshore and one onshore petroleum provinces (Fig. 3); for each play, in-place gas hydrate resources were estimated. Estimates for each of the 11 plays were aggregated to produce the estimate of total gas-hydrate resources in the United States. The offshore petroleum provinces assessed consist of the U.S. Exclusive Economic Zone (EEZ) adjacent to the lower 48 States and Alaska. The only onshore province assessed was the North Slope of Alaska, which included State water areas and some offshore Federal waters. The provinces shown in figure 3 are geographic in character; however, their formation represents an attempt to group the individual petroleum provinces along broad geologic lines. Maps depicting the geologic data required for this hydrate assessment have been included in the U.S. Geological Survey 1995 National Oil and Gas Assessment CD-ROM (Gautier and others, 1995). Maps of bathymetry, sedimentary thickness, total organic carbon content of the sediments, seabed temperature, geothermal gradient, and hydrate stability zone thickness have been published on the Assessment CD-ROM for all four offshore provinces assessed. Maps depicting the thickness of the onshore gas-hydrate stability zone in northern Alaska are also included in the Assessment CD-ROM.

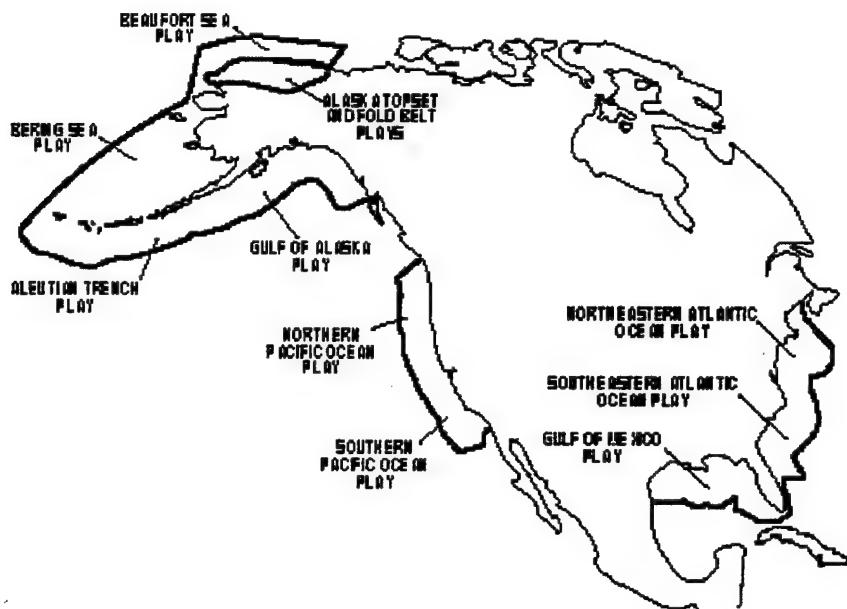


Figure 3. Gas hydrate play map of the United States (Collett, 1995).

The estimates of in-place gas-hydrate resources included in this report are presented in the form of complementary cumulative probability distributions (Table 1). These distributions summarize the range of estimates generated by assessment computer programs as a single probability curve in a "greater than" format (figure 4). Our estimates are reported at the mean and at the 95th, 75th, 50th, 25th, and 5th fractiles (table 1). We consider the 95th and 5th fractiles to be "reasonable" minimum and maximum values, respectively.

Estimated in-place natural gas resources (trillions of ft ³)						
Provinces/Plays	Mean	F ₉₅	F ₇₅	F ₅₀	F ₂₅	F ₅
Atlantic Ocean Province						
NE Atlantic Ocean play	30,251	0	0	14,128	49,448	109,491
SE Atlantic Ocean play	21,580	6,464	11,656	17,660	27,196	49,448
Gulf of Mexico Province						
Gulf of Mexico play	38,251	11,444	20,839	31,435	49,448	88,300
Pacific Ocean Province						

Northern Pacific play	53,721	16,035	29,315	45,916	67,108	123,619
Southern Pacific play	7,350	0	0	0	0	63,576
Alaska Offshore province						
Beaufort Sea play	32,304	0	0	15,188	52,980	116,555
Bering Sea play	73,289	0	0	34,613	120,087	264,899
Aleutian Trench play	21,496	0	0	0	0	183,663
Gulf of Alaska play	41,360	0	0	0	0	257,835
OFFSHORE TOTAL	319,632	112,346	190,709	275,482	397,936	675,503
Alaska Onshore province						
Topset play--State lands & waters	105	0	0	0	0	388
Topset play--Federal waters	43	0	0	0	0	161
Fold Belt play--State lands & waters	414	0	0	0	490	1,914
Fold Belt play--Federal waters	28	0	0	0	33	128
ONSHORE TOTAL	590	0	0	236	668	2,357
UNITED STATES TOTAL	320,222	112,765	191,261	276,119	398,626	676,110

Table 1. Estimates of in-place gas resources within gas hydrates of the United States (Collett, 1995).

In-place gas resources within the gas hydrates of the United States are estimated to range from 112,765 to 676,110 trillion cubic feet of gas, at the 0.95 and 0.05 probability levels, respectively (Fig. 4). Although these ranges of values show a high degree of uncertainty, they do indicate the potential for enormous quantities of gas stored as gas hydrates. The mean in-place value for the entire United States is calculated to be 320,222 trillion cubic feet of gas. This assessment of in-place gas hydrates represents those deposits that constitute the resource base without reference to recoverability.

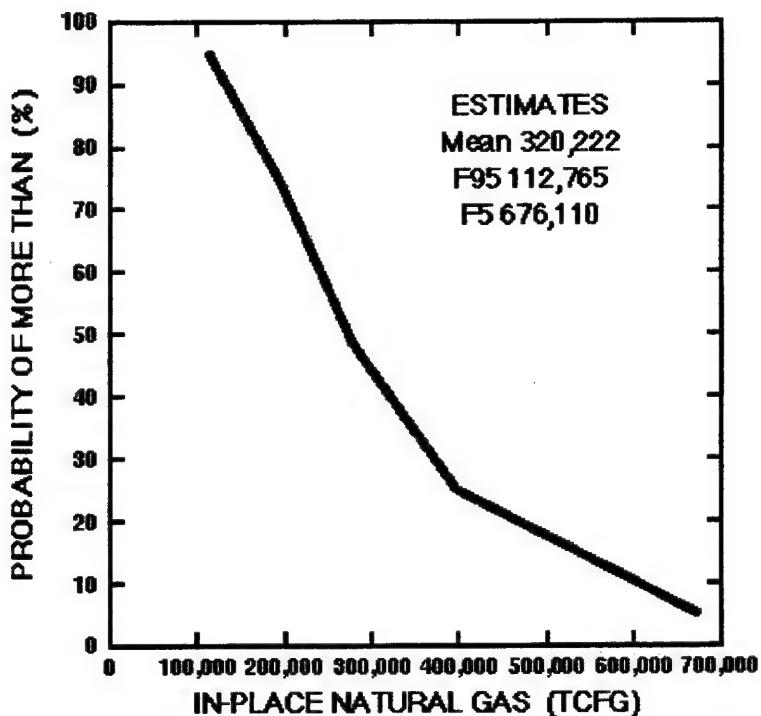


Figure 4. Cumulative probability curve showing estimated in-place gas resources within the gas hydrates of the United States. The curve is read as follows: there is a 95 percent chance that the gas hydrate resource potential is greater than 112,765 trillion cubic feet of gas (TCFG), and there is a 5 percent chance that the gas hydrate resource is greater than 676,110 trillion cubic feet of gas (TCFG) (Collett, 1995).

It is important to note that recent marine research drilling by the Ocean Drilling Program (ODP Leg 164) within the US-EEZ along the eastern margin of the United States has confirmed the occurrence of substantial quantities of methane stored as solid gas hydrate and as free-gas trapped below the gas hydrates on the Blake Ridge (Shipboard Scientific Party, 1996).

Gas Production From Gas Hydrates

Proposed methods of gas recovery from hydrates usually deal with dissociating or "melting" in-situ gas hydrates by either (1) heating the reservoir beyond hydrate formation temperatures, (2) decreasing the reservoir pressure below hydrate equilibrium, and (3) injecting an inhibitor, such as methanol or glycol, into the reservoir to decrease hydrate stability conditions. Gas recovery from hydrates is hindered because the gas is in a solid form and because hydrates are usually widely dispersed in hostile Arctic and deep marine environments. Fairly simple thermal stimulation models have been developed to evaluate hydrate gas production from hot water and steam floods, which have shown that gas can be produced from hydrates at sufficient rates to make gas hydrates a technically recoverable resource. However, the economic cost associated with these types of enhanced gas recovery

techniques would be prohibitive. Similarly, the use of gas hydrate inhibitors in the production of gas from hydrates has been shown to be technically feasible, however, the use of large volumes of chemicals such as methanol come with a high economic and environmental cost. Among the various techniques for production of natural gas from in-situ gas hydrates, the most economically promising method is considered to be the depressurization scheme. The Messoyakha gas field in the northern part of the West Siberian Basin is often used as an example of a hydrocarbon accumulation from which gas has been produced from in-situ natural gas hydrates. Production data and other pertinent geologic information have been used to document the presence of gas hydrates within the upper part of the Messoyakha field (Collett, 1992). It has also been suggested that the production history of the Messoyakha field demonstrates that gas hydrates are an immediate producible source of natural gas and that production can be started and maintained by conventional methods. Long-term production from the gas-hydrate part of the Messoyakha field is presumed to be achieved by the simple depressurization scheme. As production began from the lower free-gas portion of the Messoyakha field in 1969, the measured reservoir pressures followed predicted decline relations; however, by 1971 the reservoir pressures began to deviate from expected values. This deviation has been attributed to the liberation of free-gas from dissociating gas hydrates. Throughout the production history of the Messoyakha field it is estimated that about 36 percent (about 183 billion cubic feet) of the gas withdrawn from the field has come from the gas hydrates (Collett, 1992). Recently, however, several studies suggest that gas hydrates may not be significantly contributing to gas production in the Messoyakha field (reviewed by Collett and Ginsburg, 1997).

International Research Activities

In the last two years government agencies in Japan, India, and South Korea have begun to develop hydrate research programs to recover gas from oceanic hydrates. One of the most notable gas hydrate projects is underway in Japan, where the Japan National Oil Corporation (JNOC), with funding from the Ministry of International Trade and Industry (MITI), have launched a five year study to assess the domestic resource potential of natural gas hydrates. In numerous press releases, MITI has indicated that "methane hydrates could be the next generation source of producible domestic energy". In 1996, JNOC conducted seismic, gravity, and magnetic surveys off the northern and southeastern continental margins of Japan. JNOC will also drill a gas hydrate test well in the Nankai Trough area, near Tokyo, in 1999. As much as 1,800 trillion cubic feet of gas may be stored within the gas hydrates of the Nankai Trough. Recently, JNOC has also entered into a cooperative agreement with the Geological Survey of Canada and the U.S. Geological Survey to drill an onshore permafrost associated gas hydrate test well in the Mackenzie Delta of northern Canada in early 1998.

India, like Japan, finds itself among the countries that have to pay a very high price for imported LNG have also initiated a very ambitious national gas hydrate research program. In March, 1997, the government of India announced new exploration licensing policies which included the release of several deep water (>400m) lease blocks along the east coast of India (between Madras and Calcutta). Preliminary interpretations of recently acquired seismic data have revealed evidence of widespread gas hydrate occurrences throughout the proposed lease blocks. Also announced was a large gas hydrate prospect in the Andaman Sea, between India and Myanmar, which is estimated to contain as much as 211 trillion cubic feet of gas. The government of India has indicated that gas hydrates are of "utmost importance to meet their

growing domestic energy needs". The National Gas Hydrate Program of India calls for drilling of as many as five gas hydrate test wells by the end of this century.

Despite the fact that we know relatively little about the ultimate resource potential of natural gas hydrates, recently completed resource assessment studies and the national gas hydrate research programs of Japan and India will significantly contribute to our understanding of the technical challenges needed to turn this enormous resource into a economically producible reserve.

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Gas Hydrates and Global Change: A Northern California Case Study

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Abstract

We have carried out an ROV and hydrocast survey in the Eel River Basin offshore from northern California where Brooks et al. (1991) reported gas hydrates in near-surface sediments at water depths between 510 and 642m. They recovered and analyzed numerous hydrate specimens from piston cores, but were not able to provide the companion hydrographic data that would enable calculation of the stability of the material, nor provide indication of the ventilation age of the overlying water. This we have now been able to do.

We took part in dives 1298, 1300, and 1306 of the ROV Ventana, operated by the Monterey Bay Aquarium Research Institute, on August 20, 22 and 26, 1997. Our chosen dive location was $40^{\circ} 47'08''N$ $124^{\circ} 35'33''W$, where Brooks et al. (1991) reported obtaining hydrate samples in two adjacent cores at 512 and 518m water depth. We could not locate a depth of 512m near this site, but were soon able to discover a site at 521m depth with black mud densely populated with chemosynthetic vesicomyid clams, and with gas bubbles emerging from at least three small vents each surrounded by a white/gray halo. Gas emission was variable; it was not intense when observed on Dive 1298, was not observed on Dive 1300, and was intense on Dive 1306 at which time a sample was recovered. The area was surrounded by extensive carbonate slabs and material resembling bacterial mats. We were not able in this brief dive to confirm the presence of hydrates, but the characteristics, and very close proximity, of this site to the earlier reported finding leads us to believe that this represents the target area for study. Further exploration within about 400m of this site lead to the finding of more carbonate slabs and clam fields, but not active gas venting.

The water column in the area was characterized by bottom temperatures at 521m of 5.9, and 5.6, degrees on the first two days. These P/T values indicate that, at 5.9 degrees, the system is within 0.1 degrees of the pure methane hydrate stability point, and therefore marginally stable. The spread of 0.3 degrees between the two dives indicates very substantial eddy fluctuations at this location. Most discussions of gas hydrate stability relative to global change (e.g. Kvenvolden, 1993) necessarily take pure methane hydrate as the test case, and this site is clearly at, or now episodically beyond, this dissociation point. It is important to note that the incorporation of trace gas species, such as H₂S, into the methane hydrate matrix can confer enhanced stability.

We have obtained vertical profiles of the chlorofluorocarbon distributions in the overlying water. From the CFC-11 and CFC-12 concentrations, we estimate the pCFC apparent age of the waters bathing the exposed hydrates as ~20 years. Bottom water at this site showed density (σ theta) close to 26.8, just below the boundary of the densest waters outcropping in the North Pacific. The pCFC apparent ages at this site are consistent with the basin scale

distributions in the North Pacific on this density surface reported by Warner et al. (1996).

In summary, we have located a site of gas venting, and intense biological activity, at 521m depth, at a location where surface exposed gas hydrates have previously been reported. This site is poised within 0.1 degrees of the dissociation point of methane hydrate at the time of our observations, and is subject to eddy perturbations of at least 0.3 degrees. The ventilation age of the overlying waters is approximately 20 years, and therefore the site is probably susceptible on short time scales to global warming. Establishing the trace gas composition of the hydrate, and understanding the local eddy field, will help place firmer limits on this.

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**USGS Marine and Coastal Geology Program Gas Hydrate Research Project -
Resource Potential and Environmental Effects**

W.P. Dillon

Project organization and efforts

The project is a field and laboratory study of gas hydrate in the marine environment, divided into three main efforts: 1. studies of field relationships using seismic/acoustical data, 2. geochemical analyses, and 3. physical tests of natural and lab-formed hydrate-bearing sediments.

1. Seismic reflection profiling/sidescan sonar studies (Woods Hole Massachusetts and Menlo Park California) have advanced from mapping of the Atlantic margin to a focus on the Blake Ridge, a sedimentary accretionary drift deposit that contains the greatest concentration of gas hydrate on the U.S. Atlantic margin. Specialized seismic reflection/refraction studies on the Blake Ridge were accomplished in conjunction with an Ocean Drilling Program hydrates drilling Leg 164. Seismic work has been initiated in the Gulf of Mexico.
2. Geochemical studies (Menlo Park, California) examine the nature of natural gas hydrates obtained from drilling and compare the properties of synthetic and natural gas hydrate to those formed artificially in both deep sea and laboratory settings.
3. Physical testing studies (Woods Hole, Massachusetts) focus on identifying factors that promote concentration of gas hydrates and on the fundamental nature of hydrate occurrence, as well as on improving field mapping capabilities. Our GHASTLI (Gas Hydrate And Sediment Laboratory Instrument) system, is unique in the world at this time, for testing gas hydrate in sediment at simulated deep-sea conditions. Acoustic (P and S-wave) and electrical resistivity data, are acquired using preserved, natural, gas hydrate-bearing sediment from Ocean Drilling Project sites, and also using gas hydrate formed in place in sediment within the GHASTLI chamber. Shear strength under various conditions also can be measured. Gas hydrate growth, habit and distribution is studied in various sediment types under different simulated water depths and overburden thicknesses. Further development will allow thermal conductivity of gas hydrate-bearing sediments to be measured and the bulk variability in thermal conductivity associated with different forms of hydrate occurrence to be determined.

Project Goals

1. **To learn about natural hydrate relationships, distribution, and controls using seismic data.**
 - How much gas hydrate exists?
 - How is gas hydrate distributed in sediments?
 - How is its distribution best analyzed by seismic data?
 - What geological conditions control gas hydrate accumulation?
 - What geological conditions may influence gas extraction?
 - How do gas hydrate processes affect sediments (creating landsliding, faulting, etc.)?

2. To understand the effect of hydrate on the physical properties of sediments.

- What laboratory techniques are required to simulate gas hydrate-bearing marine sediments?
- What are the acoustic characteristics of hydrate-bearing sediments? How can these be modeled to allow the use of seismic data for mapping gas hydrates in natural sediments?
- What are the acoustic and electrical resistivity changes that are caused by hydrate formation and how can they be correlated to well logging data?
- How does formation and breakdown of gas hydrate affect sediment strength and how does this relate to slope stability and gas recovery?
- What is the effect of gas hydrate on thermal conductivity in sediments ?
- What are the rates of dissociation and how does this affect pore pressure?
- What would be the escape rates of methane to the atmosphere?

3. To understand the geochemistry of gas hydrate.

- What is the composition of gases in the gas hydrate stable zone and beneath it? How does this composition affect the stability of natural gas hydrate?
- What is the ionic composition of water in gas hydrate? Do we anticipate problems in the disposal of this water during gas hydrate production?
- What is the content of gases in gas hydrate, particularly the energy gas, methane? What is the volume ratio of gas to water?
- What is the source of the gas; where has it come from? What are the most likely generation and migration pathways?
- Do laboratory-synthesized gas hydrates provide proper surrogates for natural gas hydrates in studies of chemical and physical properties?

4. To understand the effect of geologic setting, geologic processes and host sediment properties on gas hydrate concentration and distribution.

- How can geologic processes alter or promote gas hydrate concentration?
- Do site pressures and temperatures influence the concentration potential of gas hydrates?
- What criteria can we use to search for hydrate-rich sediment?

Organization and principal researchers

1. Geochemistry

Keith Kvenvolden

Tom Lorenson

2. Physical properties studies

Jim Booth

Bill Winters

3. Field studies using seismic methods

Bill Dillon (Project Chief)

Alan Cooper

Pat Hart

Ingo Pecher (Postdoctoral Fellow)

FIELD STUDIES

Field studies use seismic reflection profiling and sidescan sonar to study natural hydrate relationships, distribution, and controls.

- How much gas hydrate exists?
- How is gas hydrate distributed in sediments?
- How is its distribution best analyzed by seismic data?
- What geological conditions control gas hydrate accumulation?
- What geological conditions may influence gas extraction?
- How do gas hydrate processes affect sediments (creating landsliding, faulting, etc.)?

PHYSICAL PROPERTIES STUDIES

Laboratory efforts use GHASTLI to measure physical properties of gas hydrate-sediment mixtures (natural and artificial). Determine effect of hydrate on the acoustic, electrical, thermal, and strength properties. Duplicate the natural environment as closely as possible.

- What laboratory techniques are required?
- What are the acoustic characteristics of hydrate-bearing sediments? How can we relate these to seismic data?
- What are the acoustic and electrical resistivity changes that are caused by hydrate formation and that can be related to well logging data?
- How does formation and dissociation of gas hydrate affect sediment strength and relate to slope stability and gas recovery?
- What are the rates of gas hydrate dissociation and how does this effect pore pressure?
- What might be escape rates of methane to the atmosphere?
- What is the effect of gas hydrate on thermal conductivity in sediments ?

GEOCHEMISTRY

- What is the composition of gases in the gas hydrate stable zone and beneath it?
- How does this composition affect the stability of natural gas hydrate?
- What is the ionic composition of water in gas hydrate? Could there be problems in the disposal of this water during gas hydrate production?
- What is the volume ratio of gas to water?
- What is the source of the gas; where has it come from? What are the most likely generation and migration pathways?
- Are laboratory-synthesized gas hydrates different from natural ones in chemical and physical properties?

SYNTHESIS

Needed to understand the effect of geologic setting, geologic processes and host sediment properties on gas hydrate concentration/distribution, possibilities of gas extraction, seafloor stability, and influence on climate.

- What sediment properties control gas hydrate habit and distribution?
- How can geologic processes affect gas hydrate concentration?
- What criteria can we use to search for hydrate-rich sediment?
- What natural conditions favor the possibility of gas extraction from gas hydrate?

What conditions decrease the feasibility of extraction or represent hazards?

- What natural processes may result in climate influences related to methane hydrate?

Significance of Gas Hydrates on the Gulf of Mexico continental slope

R. Sassen

The Gulf of Mexico represents an important case history showing how gas hydrates impact deep-water exploration and exploitation. A belt of sea-floor gas hydrate occurrences has been mapped across the upper continental slope offshore Louisiana at water depths in the 426-2200 meter range. Hydrates are preferentially distributed over salt and fault-related hydrocarbon migration conduits, often near known oil and gas discoveries such as Mars. Hydrates and oil seeps predict where new deep water oil discoveries will be made.

All three documented hydrate crystal structures occur in the Gulf. Unusual structure II and structure H hydrates contain hydrocarbons from thermogenic gas, and are associated with oil seeps. Because of the wide stability range of thermogenic hydrates, they occur in association with oil seeps across the entire slope. Structure I hydrate composed of biogenic methane is stable at lower temperatures and greater pressures, and only occurs from the middle slope to the abyssal plain. Gas hydrates are a future source of environmentally friendly fuel from the Gulf, and elsewhere. Worldwide, gas hydrates represent a much larger resource than combined reserves of oil, gas, coal, tar sands, and oil shale.

Hydrates outcrop on the sea floor, forming mounds in association with chemosynthetic communities. Using research submersibles we have been able to study hydrates at the deep sea floor, and recover intact samples for sophisticated molecular and isotopic analyses. Moreover, we have been able to rapidly manufacture gas hydrates at the sea floor from natural vent gases. Hydrate compositions are impacted by factors including source gas composition, fluctuating sea floor temperatures, and bacterial activity.

The compositions and properties of natural and experimental hydrates from the Gulf are often not predictable by simple laboratory simulations, or computer models of hydrate formation. Unusual thermogenic gas hydrates could cause pipeline plugging at higher temperatures and at more rapid rates than expected.

The Gulf of Mexico appears to be an important locality for these reasons:

1. The Gulf of Mexico is a natural laboratory for study of gas hydrates, and already has an enormous amount of geophysical, geological, geochemical, and biologic data available. There is context. The area is CONUS.
2. Gas hydrates are abundant across the Gulf from 425->2250 m water depth. Gas hydrate locations are mapped.
3. Hydrates outcrop on the sea floor, making them cost-effective to sample and study in-situ. The hydrates at the sea floor show tremendous variation, and the causes of the variation remain poorly understood.
4. Sampling equipment and protocols for research submarines and piston-core equipment exist.
5. All three known hydrate structures (I, II, and H), plus possibly undiscovered structures exist in the Gulf. There is depth zonation between hydrate types.
6. Gas hydrate research has focused on the Gulf since 1983. The first discoveries of structure

II and H hydrates in nature were made in the Gulf.

7. There are university researchers willing to cooperate to extend hydrate research in the Gulf.
8. Energy companies are intensively exploring the Gulf, and could be another source of information and funding.

Gas Hydrates in Subduction Zones

M. Kastner

1. Synthesis based on areas covered: Subduction zones (or Convergent margins)

Peru, California, Cascadia, Costa Rica, Japan, Barbados. At each gas hydrate is present, regardless of the presence of a BSR

2. Evidence in cores for presence of gas hydrate if not recovered

- Geophysics - BSR if present, etc.
- Geochemistry - High CH₄ coincident with low Cl
- Temperature of cores of -0.5 to -2.
- Soupy horizons in the cores

3. Composition and gas Occupancy

• Mostly methane, some ethane in Cascadia (in Costa Rica propane is excluded), observed low concentrations of CO₂ ~ N₂ - often caused by air contamination The volumetric ratio of methane to water is 100 in Peru and 120 to 140 in Costa Rica where the ratio increases with depth.

4. Occurrence & Distribution

1. Massive - associated with faults or lithological boundaries
2. Cement - in coarse sediments including volcanic ashes
3. Dissemination - in clays and fine silts .
4. Distribution relative to BSR: C1 concentration data suggest an overall increase toward the BSR.

5. Occurrence of gas hydrates at seafloor indicates advection. There is geochemical evidence for advection at 3 regions where gas hydrates exist at or close to seafloor, at Cascadia, Barbados, and off NW California. Evidence for paleo-BSRs - adjusted to tectonics, and/or climate (ice ages) is clearly available at least at Cascadia

6. Evidence for advection of CH₄ (intense advection through faults)

- 0~3 C of dissolved inorganic carbon, for example at Cascadia Site 892 and other sites.
- Higher hydrocarbons observed at Cascadia & Costa Rica (mostly associated with faults) . Low C~/C2

Regional advection in Costa Rica = both fault related and disseminated

7. Origin of methane

Advection versus in-situ formation, depends on geothermal gradient and tectonics

8. How much present ? Expect more in advective than diffusive geologic systems. C1 concentration if interpreted properly could be an excellent quantitative tool. We know what needs to be developed to be able to use C1 data properly.

9. How much CH₄ escapes to atmosphere from ocean? As yet unknown, need to start measuring it.

Funded Hydrate Research:: Vehicles for Future Hydrate Applications

E. D. Sloan, Jr

I Motivation for Funded Hydrate Research

A. Prevention and Remediation of Blockages

1. Well Drilling (Westport JIP)
 2. Offshore Lines/Platforms (Deepstar, Rogalands, and CHR JIP's)
 3. Production Equipment (Calgary, Pittsburgh, CSM, GPA, GRI)
- B. Storage and Separations of Gas

B. Storage and Separation of Gas

1. Peak Shaving in Gas Caverns (RD Shell and Gasunie)
 2. Storage/Shipping in Small Fields (Britgas, NTNU&Rogalands, AGIP)
 3. Separations in Biochemicals (NSF-Tulane)
- C. Modern and Ancient Climate Concerns

C. Modern and Ancient Climate Concerns

1. CO₂ Stack Gas Storage as Ocean Hydrates (Ship Rsch Inst - Japan)
 2. CH₄ Evolution from Ocean Hydrates (European Science Foundation)
 3. Air Hydrates in Antarctic Ice (Hokkaido U., Hokkaido Rsch Inst)
- D. Oceanic Hydrates and Energy Recovery

D. Oceanic Hydrates and Energy Recovery

1. In-Situ Recovery (MITI, Can Geol Surv, USGS, DoE/Pittsburgh U.)
2. Oceanic Deposits (UNC, Texas A&M GERM, A&M Petr Eng. JIP, USGS, MBARI, RI Ocean Min, St. Petersburg, SCRIPPS, NRL)

II. Fundamental Knowledge Research

A. Hydrate Characterization (Thermodynamics & Kinetics)

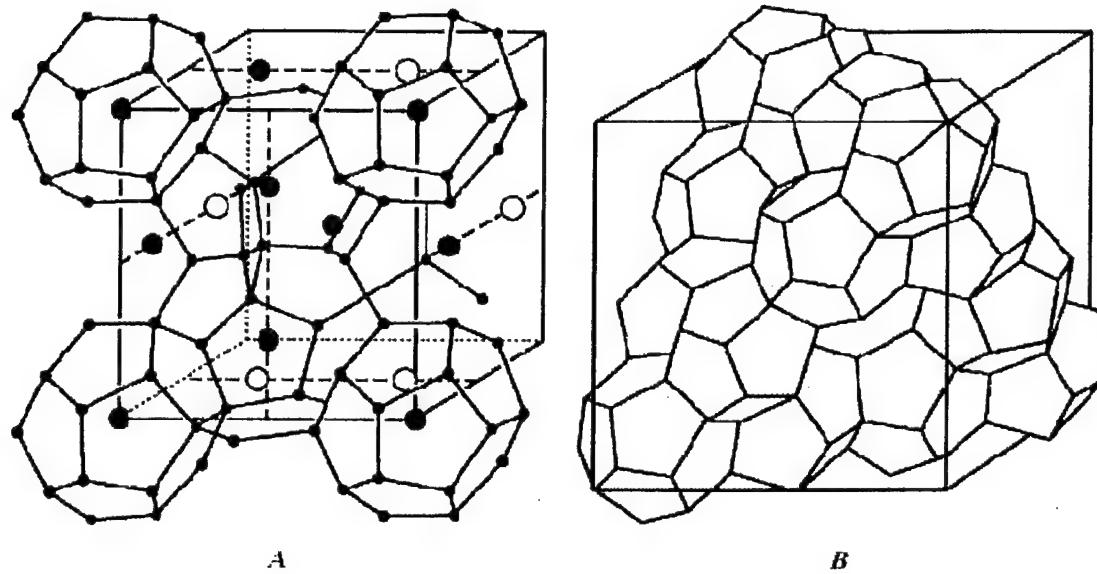
1. Sample Preparation, Annealing, and Ice Preserv. (USGS Menlo Park)
2. Neutron Diffraction (NRC Canada, Deepstar JIP-Kings)
3. NMR Spectroscopy (NRC Canada, NSF-CSM)
4. Raman Spectroscopy (NSF-CSM)
5. Simulation (NRC Canada, U. Kyoto, Reading,) B. New Hydrate Structures (in addition to 4 known)

B. New Hydrate Structures (in addition to 4 known)

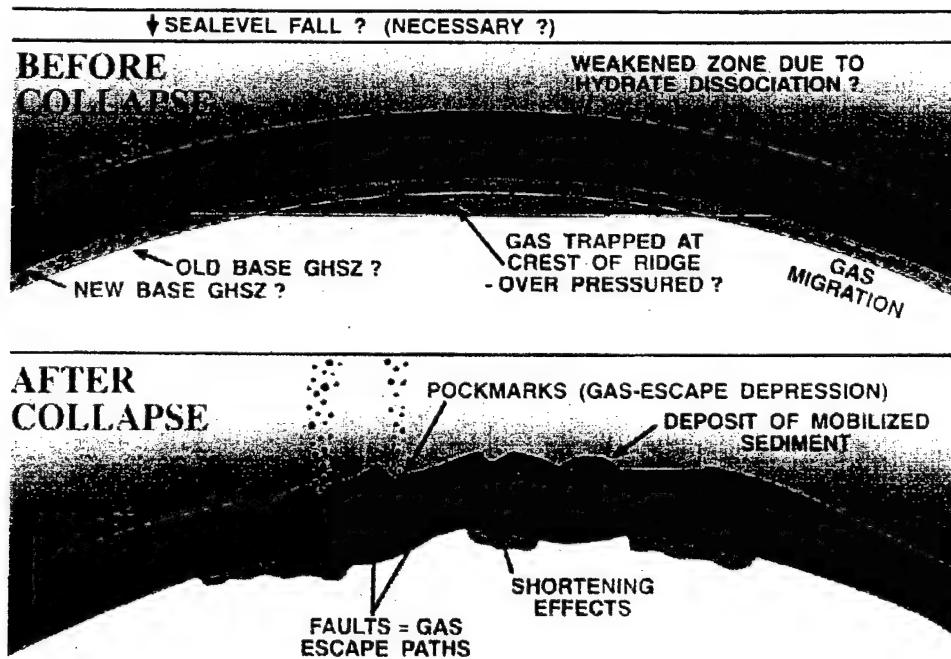
1. Hi Pressure Experiments (Novosibirsk - ISF)
2. X-Ray and Neutron Diffraction (NRC Canada)

III. Research Lessons: Hydrate Recovery Will Become Vital with Resource Scarcity

- A. Hydrates Represent the Earth's Largest Untapped Energy Reserve
- B. Hydrate Problems Provide Research Vehicles for Fundamental Research
- C. Future Applications will Build on Fundamental Research
- D. Laboratory Hydrates are not Similar to In-Situ Hydrates
- E. Hydrate Phase: almost Never Measured in Experiments
- F. Time-Independent (Thermodynamic) Properties Mostly Known for sI and sII
- G. Hydrate Time-Dependence (Kinetics) is Largest Unknown



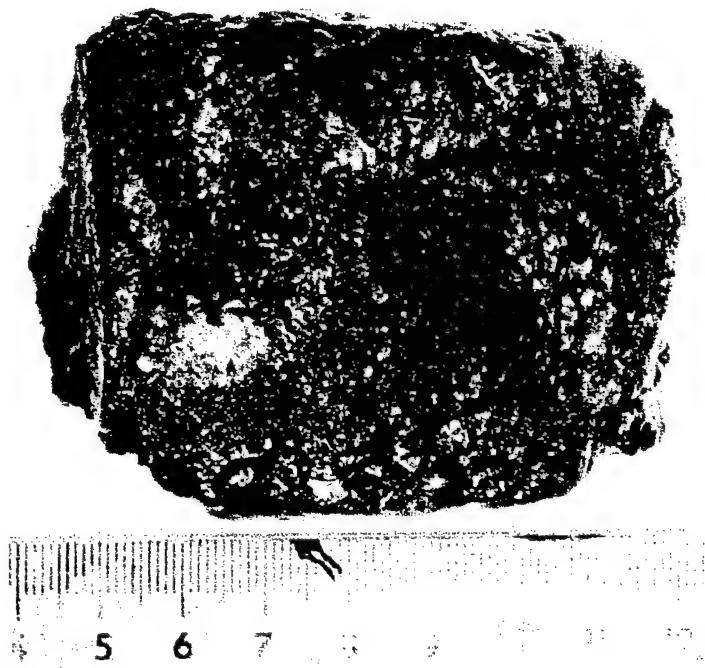
Two gas hydrate crystal structures. Red molecules, methane; Blue molecules and bonds, H₂O. A. Structure 1, body centered cubic lattice for methane hydrate, B. Structure 2, one of a number of other structures that house outer guest molecules.



Bathymetric and sub-hydrate stability zone equivalent of a geological structural culmination capable of trapping subjacent methane gas. Upper, pool of trapped gas defining an economic target. Lower, after blow-out of overpressured gas. Accumulation and release of methane involving the oceanic hydrate system is part of a long-standing process. From W.P. Dillon.



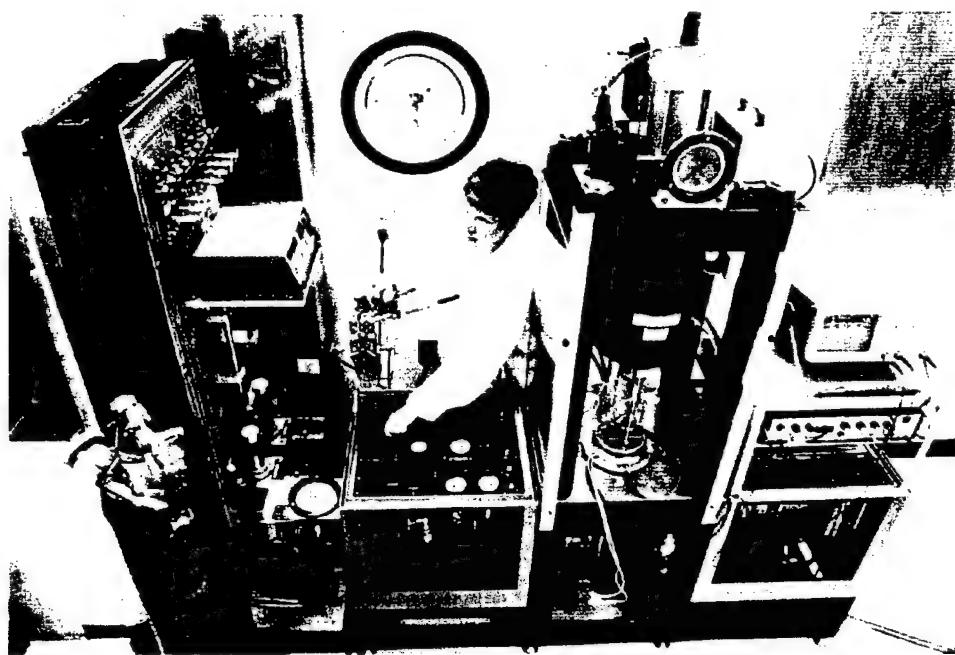
At ODP Drill Site 892, the methane hydrate is concentrated in particular horizons, which may have been originally more porous and permeable. . Photo by M. Kastner.



Sediment cemented by methane hydrate off Peru, ODP Drill Site 688, Leg 112. Photo by M. Kastner.



Massive CH₄-H₂S mixed hydrate, ODP Drill Site 892, Leg 146, off Oregon coast. Photo by M. Kastner.



'GHASTLI', the U.S. Geological Survey apparatus at Woods Hole, MA for fabricating gas hydrate in analog marine sediment pressure vessels instrumented for physical properties. Photograph by W.P. Dillon.

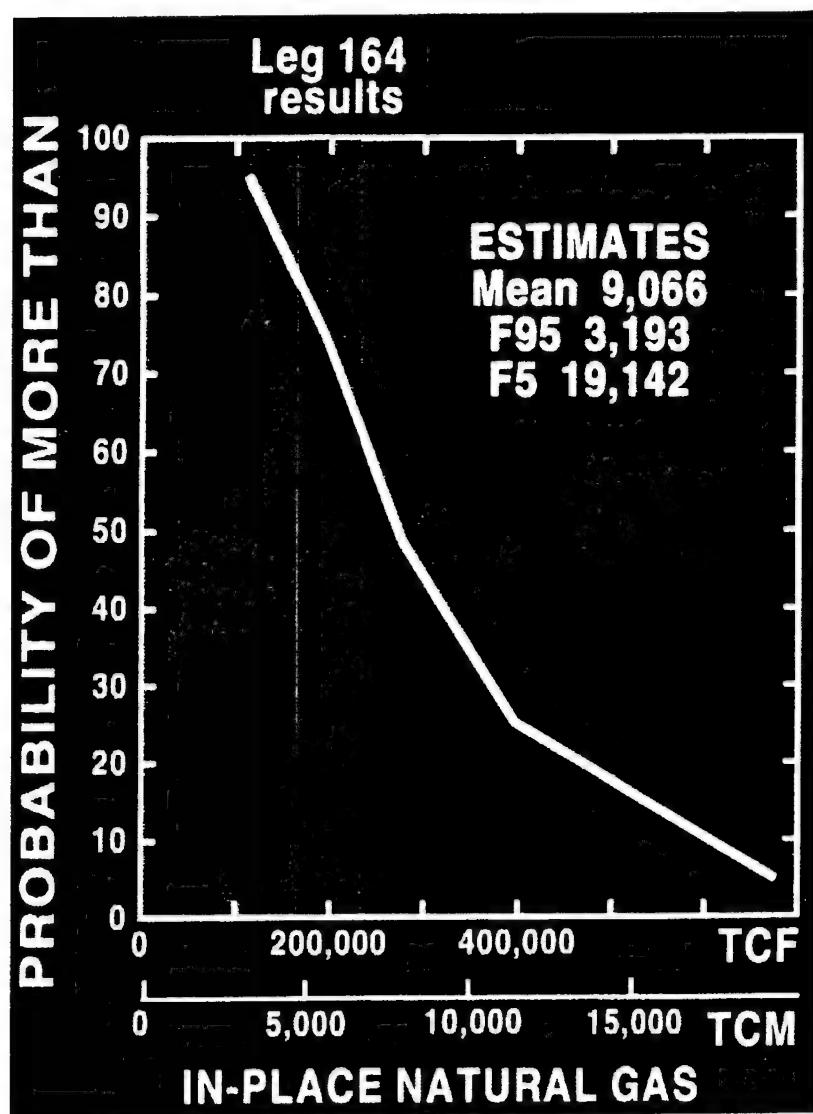
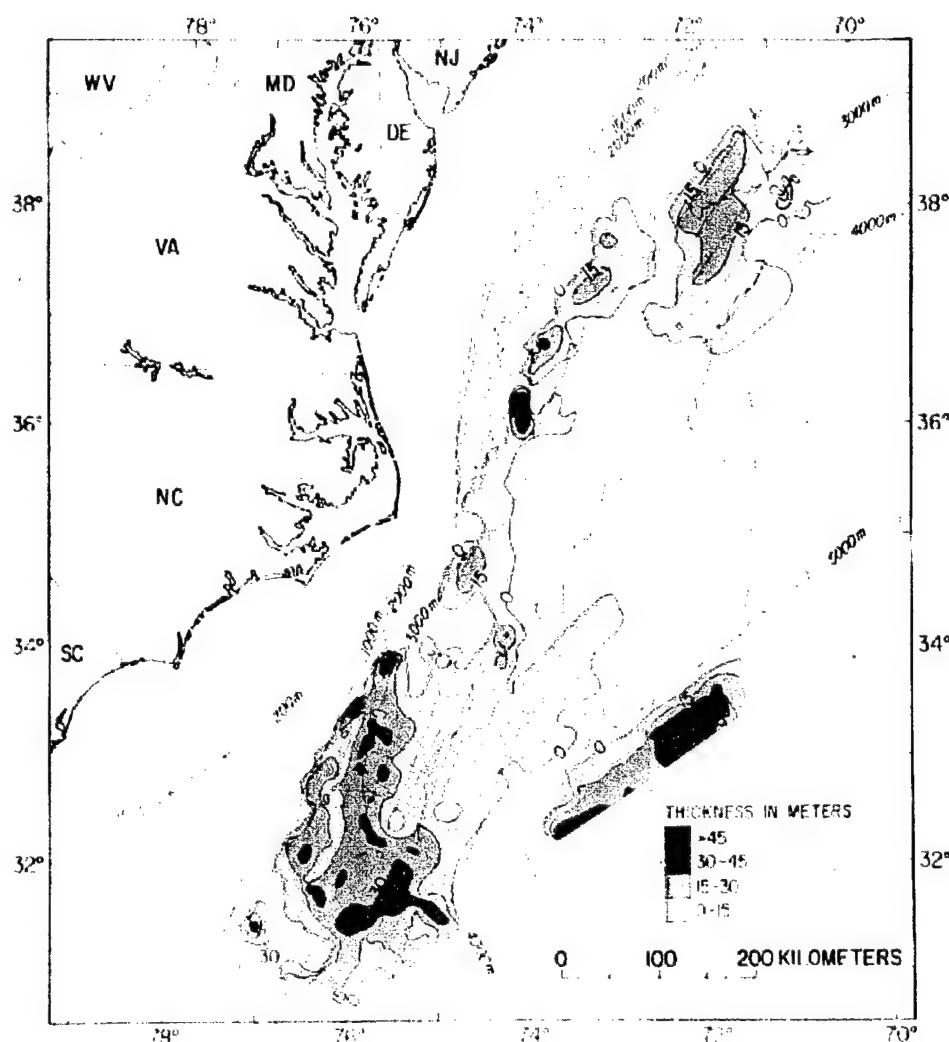


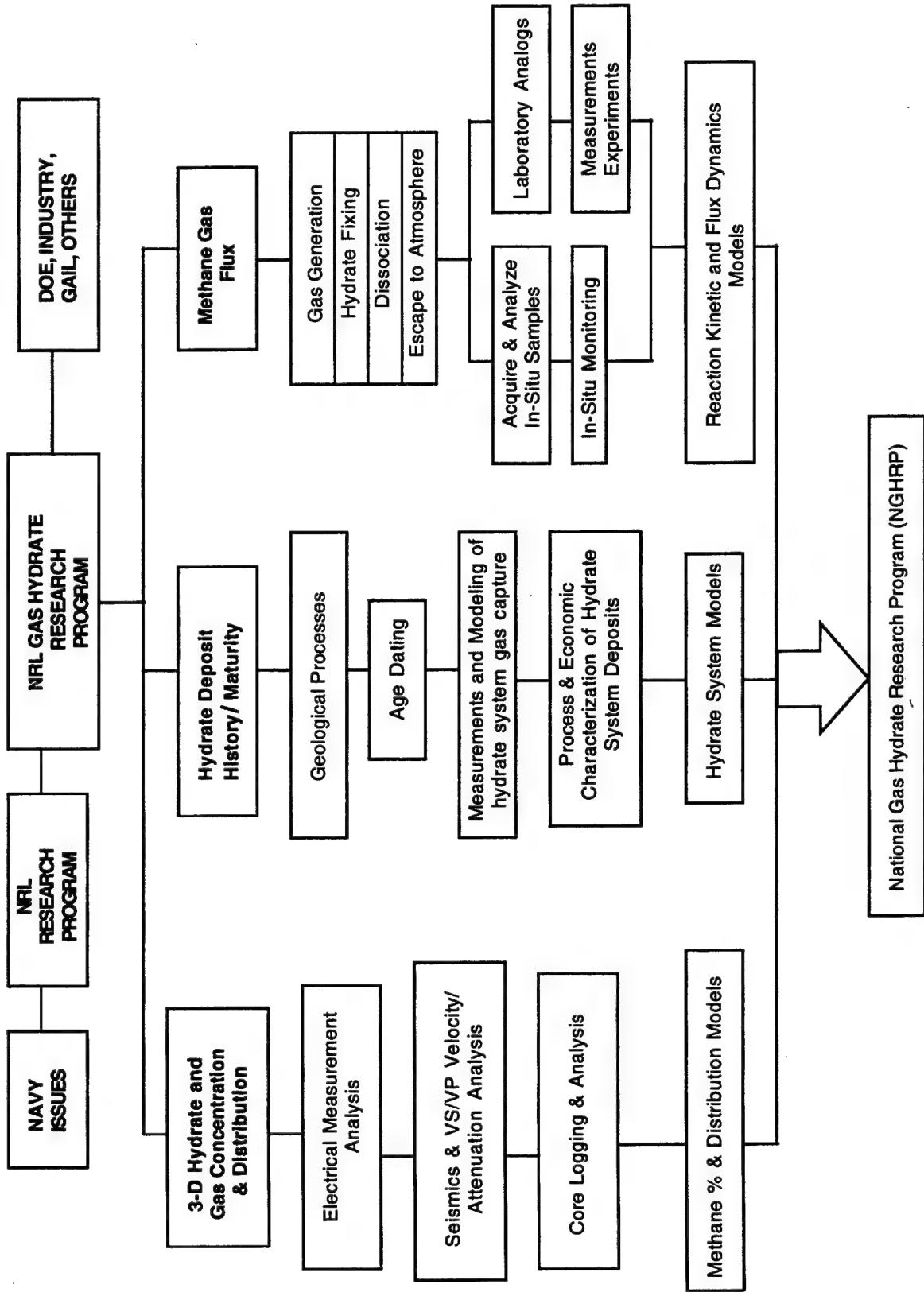
Figure 1. Estimates of methane in gas hydrate and related gas deposits for the entire U.S. EEZ. After T. Collet. The red bar shows the best volume estimate.



Map of hydrate deposits off the central U.S. east coast. Original map from seismic reflection data by U.S. Geological Survey, Woods Hole, MA. Supplied by W.P. Dillon.



Seismic profile across the Blake Ridge showing extensive blanking of the acoustic impedance structure and good BSR with subjacent gas. From W.P. Dillon, U.S. Geological Survey, Woods Hole, MA.



Appendix 1. Background and status of oceanic hydrate

Oceanic methane hydrates are a major emerging research topic spanning energy resource issues, global climate change, seafloor stability, ocean acoustics, impact on deep marine biota, and a number of special topics of limited interest. Recent developments in the last five years have both broadened and deepened interest in developing hydrates as a source of methane gas.

1. Much more is known about hydrates. One of the greatest increases in knowledge of gas hydrates has probably come as a result of the Ocean Drilling Project (ODP); especially from Leg 164, which took place in November/December, 1995. This has been the only ODP leg that was devoted solely to the study of gas hydrate, although a number of other DSDP/ODP drill holes intersected hydrates. The sites were selected off the southeastern United States, where the US Geological Survey, the University of North Carolina and other academic researchers have carried out extensive hydrate studies. Four holes were drilled in the Blake Ridge region.

In the 1991 report (Max et al., 1991b), two types of knowledge gaps were identified, gaps of scale and gaps of topic. By gaps of scale was meant the tendency for geochemists to sample cores on a visual basis and thus examine hydrate at a scale of centimeters whereas geophysicists used seismic waves and examined the problem on a scale of hundreds of meters. The ODP Leg 164 work presented an opportunity to improve this situation. Although geochemistry is still sampled on a centimeter scale, more effort is being made to examine typical samples rather than the occasional obvious gas hydrate concentration. The more extensive use of well-logging methods provides a means of integrating detail measurements over the depth of the drill holes. Finally, seismic studies were very closely coordinated to the Leg 164 drilling, higher resolution seismic sources were used and efforts were made to correlate geophysical results to geochemistry, sedimentology, physical property measurements, etc. Although the Leg 164 work is the most intensive ODP effort on gas hydrate, much other ODP-related seismic and other data, especially those from the western margins of North and South America, also have been applied to studies of hydrate.

The gaps of topic (Max, 1991b) refer to the fact that, at that time, most studies either were devoted to the organic chemistry of hydrate gases or were seismic analyses that concentrated on the BSR reflection at the base of the hydrate zone. Significant advances in our understanding of the BSR and broadened efforts to use a range of seismic attributes and well logging for study of hydrates have been made in the last six years. Although this increased knowledge has been significant, interpretation of seismic data is still controversial, although we now have a much better understanding of the problem. In the past six years much more theoretical and laboratory work has been initiated regarding the formation of hydrate and physical properties of sediment/gas hydrate mixtures. This work has begun to include measurements made under deep sea conditions created in the laboratory and other laboratory simulations. The attempt to simulate deep sea conditions in the laboratory is extremely important, but also very difficult, and much more progress is to be expected. Studies of thermal characteristics and processes are providing new understanding. Recently the formation of gas hydrate in situ in the ocean has provided valuable insights. The approach of using chemical gradients to study gas hydrate seems to appear promising. Proposals to use the Cascadia hydrate deposits as a natural laboratory hold great potential and similar proposals probably should be developed for the Blake Ridge area.

2. Commercial drilling is moving into deeper waters and is encountering hydrates and hydrate stability conditions in the seafloor that do not occur in the shallower waters. Precise lateral and branching lateral drilling methodology is now being developed. Thus, at least the initial development of drilling, recovery, and pipeline technology needed to develop oceanic hydrates has been begun as a byproduct of deeper water drilling for conventional hydrocarbon deposits. This can be considered as a serendipitous economic benefit for hydrate development, although much hydrate-specific work remains to be done. As normal petroleum exploration drilling moves into the depth realm of hydrate, we are likely to experience disruptions caused by shallow gas escapes and sediment mobilizations that are fed by gas and other fluids trapped beneath the hydrate-cemented sealing layer. Such phenomena have been reported and better understanding is imperative.

3. Even conservative estimates of oceanic hydrate volumes now recognize that the potential methane resource in hydrate and related gas deposits is very large. For instance, up to 200,000 TCF of methane may exist in hydrate deposits adjacent to the continental United States (Gautier et al., 1996). A number of deposits have been characterized in detail in the U.S. EEZ based on a number of acoustic analytical techniques. Other preliminary hydrate deposit characterizations, based on the presence of Bottom Simulating Reflectors (BSR), which indicates free gas trapped beneath the hydrate, have been made along a number other continental margins.

4. Foreign governments (principally in Japan and India) have begun to develop hydrate research programs to recover methane from oceanic hydrates. The U.S. Department of Energy has plans for initiating a new hydrate research and development program in the near future. India has included hydrate development within its hydrocarbon regulatory framework for exploration and extraction.

The most advanced hydrate research and development program at present, however, is being conducted by the Japanese. AIST, the Japanese Agency of Industrial Science and Technology regards methane hydrates as a potential next-generation source of energy, and the only significant one that could be produced domestically. The Japan National Oil Corp (JNOC) has given a commitment to begin to sink test wells in oceanic hydrates (probably adjacent to Japan) no later than 1999. The earliest date that commercial production of methane hydrates could start has been estimated to be about 2010: About six trillion cubic meters of oceanic methane hydrates may exist adjacent to Japan. Recovery of one-tenth of the estimated total methane hydrate reserves extracted at relatively low cost is currently regarded as being the economic target that would produce at least about 100 years supply of natural gas for Japan.

5. A number of hydrocarbon exploration companies are taking an active interest in recovering methane from oceanic hydrates. The activity in these companies varies from in-house studies to watching briefs at present. To our knowledge, no private company has yet established a full-time research/ exploration/ extraction department to deal with hydrates. However, the interest shown is significantly greater than that of as little as five years ago, when energy companies expressed no significant interest in the commercial possibilities of hydrate.

Appendix 2. NRL Workshop Agenda

Dates: 23-24 September, 1997

Venue: 'Quarters A', Naval Research Laboratory, Washington DC.

Quarters A is a small, two-story building that used to be the Captains Quarters in the early days of NRL. It has since been converted into a small conference facility in which the participants are not disturbed by other activity.

Coffee and soft drinks will be available from 08:30 and throughout the workshop, in addition to coffee breaks, which will enhance the informal nature of the workshop.

Lunches provided by NRL to participants will be brought to the workshop on both days. Participants are also free to go to either of the NRL messes for lunch. The lunch breaks will be long enough to allow for short walks outside of the workshop venue.

Workshop Objectives

- Demonstrate NRL research potential for hydrate research
 - Outline NRL hydrate research program utilizing existing resources
 - Consider possible expansion of NRL research capabilities
 - Identify joint research activities and agencies/institutions
 - Identify potential funding sources

Workshop Organization

- Part 1.** Brief presentations
 - Part 2.** Overview and 'assignments'
 - Part 3.** Separate topic-oriented workgroups
 - Part 4.** Presentation of workshop results and general discussion
 - Part 5.** Conclusion and summary

23 September

<u>09:00</u>	<u>Welcome and introduction</u>	Dr. B. Rath
<u>09:15</u>	Part 1. Brief Presentations (10-15 minutes each)	

Dr. P. Brewer (MBARI). Modern seafloor hydrates and present a video on the most recent diving on the seafloor hydrate deposit off Monterey and will present thermodynamic calculations on hydrate stability.

Dr. K. Crane (NRL Marine Sciences Div). Modern seafloor hydrates and gas/fluid seeps off Svalbard, working with the Russians

Dr. J. Gardner (NRL Marine Sciences Div). Side-scan sonar imaging of the seafloor and image analysis as an aspect of oceanic hydrate research. Hydrates around Korea.

Dr. J. Karle (Lab. for Structure of Matter). Structure of Clathrates

Dr. M.D. Max (NRL Marine Sciences Div). Diagenetic affect of hydrate formation; material properties of the sediment-hydrate-gas reservoir.

Dr. J. Gettrust (NRL Marine Sciences Div). High resolution seismic studies of gas hydrate regimes; implications for hydrate stability and geologic processes. Areas

studied include passive margins (Blake Ridge) and active margins (Nankai Trough, Cascadia margin).

Dr. O. Diachok (NRL Acoustics Div). Full field inversion techniques for acoustic analysis pertinent to characterizing marine sediments with hydrate and gas.

Dr. W. Dillon (USGS, Woods Hole). USGS studies of oceanic hydrates, particularly along the U.S. E coast.

Dr. C. Paull (Univ. N.C). Hydrate research and ODP Leg 164.

Dr. T. Collett (USGS, Denver). Industry-style downhole-log-based gas hydrate volume analysis from Blake Ridge and extrapolation to U.S. EEZ; permafrost-related hydrates and working with the Japanese.

Dr. M. Kastner (SCRIPPS Inst.). Gas hydrates on the US west coast active margin.

Dr. R. Sassen (GERG). Gas hydrates in the Gulf of Mexico.

Dr. D. Sloan (Colorado School of Mines). Industry-funded hydrate chemical research into hydrates and the potential wider use of this information. The funding vehicle at hand must be used in order to do fundamental research which in turn has widespread applications to longer-range considerations than those of the funding vehicle.

Dr. D. Nagel (Superintendent, NRL Condensed Matter & Radiation Sciences Division). NRL Condensed Matter & Radiation Sciences Division capabilities at NRL.

Dr. J. Murday (Superintendent, NRL Chemistry Division). NRL Chemistry Division capabilities

12:30: Lunch on site

13:30: Part 2. Overview and 'assignments' Dr. B. Rath and Dr. M.D. Max

Review of Science and applied issues relating to hydrates. Funding levels and focused research.

Part 3. Separate topic-oriented workgroups. Remainder of Afternoon

Workgroup 1. Marine Sciences. Chairman, Dr. P. Brewer

Workgroup 2. Materials and Chemistry. Chairman, Dr. D. Nagel

24 September

09:00 Part 4. Presentation of workshop results and general discussion. Workshop Chairmen: presentation and joint seminar

Whole morning (It may prove practicable to begin the conclusion and summary before Lunch).

12:30: Lunch on site.

13:30: Part 5. Conclusion and summary. Dr. B. Rath and Dr. M.D. Max

16:00 Conclusion of Workshop. (The business of the workshop may be concluded before 16:00, which should be taken as the latest time for conclusion of the workshop).

Appendix 3. List Of Invitees For NRL Gas Hydrate Workshop

1. Dr. Bill Dillon
U.S. Geological Survey
Woods Hole, MA 02543
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Home tel: (508) 548-9439
<bdillon@nobska.er.usgs.gov>
2. Dr. Timothy S. Collett
U.S. Geological Survey
Denver Federal Center
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Denver, Colorado 80225 USA
[303 236-5731 / 303 236-8822]
<tcollett@bpgsvr.cr.usgs.gov>
3. Dr. Charles K. Paull
Department of Geology
University of North Carolina
Chapel Hill, NC 27599-3315
[919-962-0687 / 919-966-4519]
<paull@email.unc.edu>
4. Dr. Peter Brewer
Monterrey Bay Aquarium Research Institute
P.O. Box 628
7700 Sandholdt Road
Moss Landing Ca 95039-0628
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<brpe@mbari.org>
5. Dr. Dendy Sloan
Colorado School of Mines
Dept. of Chemical Engineering
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Golden, Colorado 80401
[303 273-3723 /]
<esloan@gashydrate.Mines.Colorado.edu>
esloan@slate.mines.edu
6. Dr. Miriam Kastner
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Scripps Institution of Oceanography
University of California, San Diego
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[619 534-2065 / 619 534-0784]
<mkastner@ucsd.edu>
7. GERC/Industry
Dr. Roger Sassen
Deputy Director
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Geochemical and Environmental Research
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Appendix 4. Potential NRL Marine CH₄ Dynamics Program

- 1. Crystalline Structure**
 - a. Mixing & trace element affects on nucleation and growth
 - b. Temperature/Pressure Stability
 - c. Osmotic Effects
 - d. Nucleation & Growth Issues, Thermodynamics, reaction rates
 - e. Molecular dynamics; first principal modeling
 - f. Hydrate crystal structures & stability
- 2. Pore Water Chemistry**
 - a. Boundaries of Hydrate Zones
 - b. Dynamics of Fluid Flow
 - c. Fluid pumping issues
- 3. Biochemistry**
 - a. Biogenic/Thermogenic Methane
 - b. Life form Dependency
- 4. Laboratory Analogies to natural occurrences**
 - a. Passive margins
 - b. Active margins
 - c. Mineral deposit development and forms
- 5. Temporal History**
 - a. Isotopic Age Dating
 - b. Hydrate Conservation Cycle
- 6. Groundwater Movement & Behavior (brine formation)**
- 7. Hydrate Tectonics/Mass Effects**
- 8. Oceanographic Issues**
 - a. Concentration Sensors
 - b. Remote Sensing
- 9. Modelling - Marine CH₄ Flux Model (Hydrate)**
- 10. Phase Chemistry &Diagrams**
- 11. Geophysical/Geological Characteristics**
 - a. Physical Properties
 - I) Remote
 - II) In Situ
 - b. Geological Structure
 - c. Setailed seismo-acoustic analysis and hydrate location/volumes
 - d. 3-D (including seafloor) characterization of HSZ (x 2.5 thickness)
- 12. Dynamics**
 - a. Measurements of Processes

- b. Historical Record
- 13. Localized vs. Diffuse Processes
- 14. Oceanographic
 - a. Sensors
 - b. Underwater hyperspectrometer?
- 15. Electrical characterization
 - a. Resistivity / Conductivity
- 16. Energy density (3-D)

NRL Gas Hydrate Program - Chemistry Issues

1. Crystalline Structure Concerns
 - a. Lattice - Site Non-methane Substitutions
 - b. Temperature/Pressure Stability of Synthetic Hydrates
 - c. Osmotic Effects
 - d. Nucleation Issues
2. Pore Water Chemistry of Hydrates
 - a. Boundaries of Hydrate Zones
 - b. Dynamics of Fluid Flow
 - c. Brine Exclusion in Confined Spaces
3. Biochemistry and Hydrates
 - a. Biogenic vs. Thermogenic Methane Source
 - b. Lifeform Dependency
 - c. Hydrate - based Ecosystems??
4. Laboratory Analogs to Natural Methane Hydrates
 - a. Replacement of Water Molecules in Lattice
 - b. Mixed-guest Hydrates
5. Temporal History of Natural Hydrates
 - a. Isotopic Age Dating
 - b. Hydrate Conservation Cycle
 - c. In-situ Methane Gas Sensor
6. Groundwater Movement & Behavior During In-situ Hydrate Formation
 - a. Brine Exclusion
7. Methane as Feedstock for Higher MW Organics; Navy Fuel
8. Methane as H₂ Transport Medium
 - a. Cracking CH (Catalysis??)